AMERICAN

CHEMICAL JOURNAL

EDITED BY

IRA REMSEN

PRESIDENT OF THE JOHNS HOPKINS UNIVERSITY

VOL. XXIX.—JANUARY–JUNE, 1903.

Contents of Vol. XXIX.

No. 3.

No. 4.

REVIEWS.

AMERICAN

CHEMICAL JOURNAL

PHYSICO-CHEMICAL INVESTIGATIONS IN THE PYRIDINE SERIES.

BY E. J. CONSTAM AND JOHN WHITE.

The idea which led us to undertake this work was the desire to ascertain in how far the regularities 'n the increase in the heats of combustion and of formation, and the determined constants for the molecular heat of evaporation, which had been observed between homologues in the fatty and in the aromatic series would be found to apply to the pyridine series.

For this purpose we undertook to prepare considerable quantities of as pure substances as could possibly be obtained, and with these to carry out investigations with the above objects in view.

This investigation eventually led us further than had been originally intended, since relations between the compounds studied appeared during the course of the work of such interest as to make it desirable not merely to confine the investigation to a study of the heat relations but to include an electrochemical study as well.

Preparation of the Pure Bases.

This has proved by no means a light task and has occupied

by far the major portion of the whole time devoted to the research. Although Ladenburg[1] and his pupils, as well as Schwarz,[2] Stoehr,[3] and others had previously prepared and described some of the properties of these bases and had outlined the general methods employed for their purification, they had occasion to prepare only a very few grams ; it proved a much more difficult task to obtain larger quantities in a state of purity such as was required for this investigation. Moreover, the properties as published by these investigators do not entirely agree in all respects, indicating possible sources of impurity in some cases.

For this reason, and that it may be seen what the condition of purity of the substances used by us was, we give here in some detail the methods employed for this purpose. These are essentially similar to those described by the investigators mentioned, differing in some minor particulars only, which will be mentioned in the proper connection. It was found that the mercuric chloride double salt was in most cases best suited to the separation and purification of the bases, being very insoluble and crystallizing well, entailing minimum loss during the repeated recrystallizations necessary, but possessing, on the other hand, the disadvantage that, on account of the high specific gravity and marked insolubility, the difficulty of working with large quantities is greatly increased.

The pyridine used was at first purified by conversion into the ferrocyanide and into the zinc salt ; it was, however, later found possible to obtain pyridine from Kahlbaum possessing a high degree of purity, such that a perfectly satisfactory product could be obtained from it by fractionation, after drying over caustic potash. While for most of the experiments the pure base obtained from the ferrocyanide was used, a comparison of the heats of combustion, as given in Table I., will show that the Kahlbaum product was practically identical in its properties with that prepared by us.

The pyridine thus obtained possesses a not unpleasant odor, boils constantly at $115°.2$ C. at 760 mm. and $0°$ C., the ther-

[1] Ann. Chem. (Liebig), **247**, 7 (1886).
[2] Ber. d. chem. Ges., **24**, 1676 (1891).
[3] J. prakt. Chem., [2], **45**, 20 (1892).

mometer entirely in the vapor.   It is strongly refractive and has a density at 15° C., calculated to water at 4° C., of 0.989305.

Although Kahlbaum furnished us also with a quite pure α-picoline, careful tests showed that it still contained minute traces of other bases.   We deemed it advisable, therefore, to subject it to further purification, and for this purpose transformed it into the mercuric chloride double salt, as described by Ladenburg, and recrystallized this from hot water containing a small amount (2 to 3 per cent) of dilute hydrochloric acid.

The purification of this salt can be easily accomplished by adopting the following procedure :   After preparing a very concentrated solution by the aid of heat, filter rapidly through a folded filter, using a stemless funnel for the purpose ; any crystals formed are again brought into solution, and the vessel set aside until crystallization sets in.   The α-picoline salt, on account of its great insolubility, soon begins to separate out in large diamond-shaped, striated prisms, which frequently attach themselves together, building up long, lance-shaped needles, terminated by one of the diamond-shaped crystals. After the greater part—but not all—of the α-picoline salt has separated out, minute, iridescent flakes are formed, settling slowly ; if at this point the mother-liquid be poured off and the operation of dissolving, recrystallizing, and pouring off be repeated, perfectly pure mercuric chloride double salt, of composition $C_6H_7N.HCl.2HgCl_2$, melting sharply and constant at 153° to 153°.5,[1] can be obtained in two to three crystallizations.

To obtain the base from this it was decomposed with double the calculated amount of sodium hydroxide in concentrated solution, the whole brought into a copper flask, and distilled over a free flame until the greater part of the liquid had distilled off, then in a current of steam, until the distillate no longer had the characteristic odor of the base and exhibited only a very faint alkaline reaction with litmus. The base was then separated from the distillate by the addition of solid caustic potash, with cooling, until a very concen-

[1] For comparison we give the values of other observers : Ladenburg and Lange, 154°.

trated potassium hydroxide solution was obtained.   The base separated as a light, transparent, oily layer at the top and was removed by means of a separatory funnel.   The potassium hydroxide solution was extracted with ether and, after distilling off the ether at the lowest possible temperature (the last portions best by means of a slow current of air), the entire amount was thoroughly dried over solid potassium hydroxide and distilled.   It showed a constant boiling-point 128°.8 C. (128°.7 and 128°.9 for two different preparations) at 760 mm. and 0° C.,[1] with the mercury entirely in the vapor. We obtained in this way, partly by repeated fractionation of a mixture of pyridine bases and use of the fraction boiling between 128° to 133°, partly starting from the Kahlbaum "pure" α-picoline, a total of 115 grams with the above boiling-point.

This α-picoline is a clear, transparent liquid, with a very marked characteristic, pyridine-like odor and a strong refractive action upon light; it volatilizes markedly and has a strong tendency to absorb water, so that it must be kept in well-stoppered flasks over solid caustic potash; it attacks cork, rubber, and other organic substances quite markedly. The density at 15° C., reduced to water at 4° C., is 0.94972.

The β-picoline which we used in our subsequent experiments was obtained from three separate sources : One portion prepared synthetically by ourselves, using Stoehr's[2] method ; a second portion, which had been previously prepared by him, was received from Mr. E. Stebler, of this laboratory, while for the major fraction we are indebted to the kindness of Prof. Stoehr himself.   To both of these gentlemen we here take the opportunity of expressing our sincerest thanks.

All of these were received in the raw condition and were subsequently purified.   The raw base contains a large number of other substances, from which it is not easy to separate it in pure condition.   The method which we made use of for this purpose was essentially that described under α-picoline, though in this case the operation required closer attention and

[1] Ladenburg, 129°; Lange: Ber. d. chem. Ges., 18, 3436, 129° to 130°; Kahlenberg : J. phys. Chem., 5, 284, 129° at 745 mm.   The latter used Schuchardt's a-picoline, without further purification.

[2] A later portion was worked over according to a method privately communicated by Prof. Stoehr, which materially lessened the time of the operation.

many more recrystallizations than was the case with the
α-compound. On account of the number of impurities pres-
ent, all of which form difficultly soluble double chlorides with
mercury, differing very little in point of solubility from that
of the β-salt, the crystallizations had to be controlled by means
of the magnifying glass, and only when an absolutely uni-
form product was obtained were we satisfied as to its purity.
This was rendered the more difficult on account of two factors
which affect the result : the β-salt does not show so marked a
crystal habit as the α-salt, but varies considerably with the
degree of concentration and the nature of the impurities pres-
ent. Generally it is obtained in the form of long, prismatic
needles, but can also be obtained in thin, friable leaflets, ap-
parently formed by the clustering of the needles ; it was also
found impossible to obtain a product crystallized from
acidulated water with a constant melting-point, although
microscopic examination showed it to be uniform in character.
We found, however, that on recrystallizing from hot alcohol
(80 to 90 per cent), in which it is quite easily soluble (though
only slightly so in the cold) a product was obtained which
melted sharply at 146° C.[1]

The difficulty in obtaining a salt of constant melting-point
from aqueous solutions is apparently due to a partial hydro-
lytic dissociation of the salt by the water present. β-picoline
belongs to a class of weak bases and its salts react acid
toward indicators, all giving the characteristic odor of the
base. In the case of the double salt with mercuric chloride,
although we constantly worked with acidulated solutions, the
odor of the base is quite pronounced. If the solid salt be
brought into water heated nearly to the boiling-point, with
the flame still under the vessel, it in part dissolves at once,
but a considerable portion sinks to the bottom and forms an
oil which only slowly dissolves, the solution meanwhile giv-
ing a very pronounced odor of the base. If the liquid be
poured off from the oil, the latter instantly solidifies to a hard
cake which is much more difficultly soluble than the original
crystallized salt, and which shows a markedly different melt-

[1] Ladenberg, 143° ; Schwarz, 147° to 149° ; Stoehr, 146°.

ing-point from the salt itself. Considerable variations in melting-point were observed with the various fractions, but all showed virtually the same when recrystallized from moderately strong alcohol. The same observation was made with the γ-picoline compounds, being even more marked in that case, since γ-picoline is a somewhat weaker base than β-picoline.

The β-picoline obtained from the mercury salt by distilling with sodium hydroxide, separating with caustic potash, and drying over solid potassium hydroxide, boiled at 143°.4 C. at 760 mm. and 0° C.,[1] with the mercury entirely in the vapor of the boiling liquid. It has a much more agreeable ethereal odor than α-picoline, and, like the latter, has a strong refractive action on light. The density at 15° C., calculated to water at 4° C., is 0.96134.

As the starting-point for the preparation of the γ-picoline we made use of a mixture of bases furnished by Kahlbaum. This was subjected to repeated fractionation, and, eventually, the fraction distilling between 128° and 133° was used in the preparation of α-picoline, as already mentioned, while the fraction 140°–146° was used for the preparation of the γ-picoline. Unfortunately, an accident deprived us of a considerable quantity of the rectified raw base, which prevented the subsequent investigations being carried out in their entirety upon this member of the picoline group.

To obtain the γ-picoline, the fraction 140°–146° was converted into the hydrochloride and fractionally precipitated, as described by Ladenburg, Mohler, etc., with mercuric chloride. The salt obtained was very impure, but was separated by subsequent recrystallizations from acidulated hot water into three principal portions : one consisting of broad leaflets, constituting about one-half of the total, and which, after several recrystallizations, melted constant at 164° to 165° ; a second portion, crystallized in small, thin leaflets, gave a melting-point of 186°.5 to 187°.5, and corresponds both in crystal form and melting-point to α, α'-lutidine, while the third portion containing the γ-picoline salt mostly, crystallized as long, thin

[1] Ladenburg, 142° to 144°; Schwarz, 143°.5; Stoehr, 143° to 143°.2 at 750 mm.

needles. It was found even more difficult to obtain a salt of constant melting-point in this case than in the case of the β-compound, and the phenomena noted there were observed in a much more marked degree : the formation of larger quantities of the oil, a more noticeable odor of the base, and a greater divergence of the melting-point from a constant. The latter fact was also noted by Mohler,[1] who states that he succeeded in bringing the melting-point from 130°, that of the original salt, to 150°, by repeated recrystallizations. This and later observations made with other salts of γ-picoline, notably with the picrate, as well as a consideration of the widely diverging values found by various investigators, leads to the conclusion that γ-picoline is a very weak base, and that hydrolytic dissociation is the cause of these discrepancies. Recrystallization from alcohol materially reduced this, though apparently not completely (the alcohol used was only about 85 to 90 per cent). The melting-point of the salt recrystallized from alcohol was 124° to 128° and showed no perceptible change on repeating the crystallization. The base obtained from this had the boiling-point 143°.1 C. at 760 mm. and 0° C.[2] The density at 15° C., calculated to water at 4° C., is 0.95714.

THERMOCHEMISTRY OF THE PYRIDINE BASES.

Although a few determinations of this sort have been made by other investigators, more especially with pyridine and α-picoline, the results obtained by the various observers are not in sufficiently close agreement to render redeterminations of these values superfluous. We have therefore undertaken to make as far as possible, with the material in hand, a complete thermochemical study of the pyridine bases. Comparison of the results obtained by us with those of other observers will be made under each group of investigations.

The room in which the determinations were made was one which had been specially constructed and arranged for such purposes, lying in an underground cellar towards the north, so situated that no direct sunlight could enter, and provided

---

[1] Ber. d. chem. Ges., **21**, 1010 (1888).

[2] Given as 142°.5 to 144°.5, Ladenburg ; 144° to 145°, Lange ; 142° to 144°, Behrmann and Hoffmann.

with double walls, doors, and windows. The temperature
was kept constant at 15° C. by means of a heater provided
with a regulating device and a sensitive thermometer, which
showed almost no appreciable deviation at any time during
the investigations. All liquids were kept in the room for a
long time before use, that they might be of uniform tem-
perature, and all the usual precautions necessary to such work
were carefully observed.

This part of the investigation may be classified under the
following heads : Heats of combustion, of formation (calcula-
ted from the former), specific heats, heats of vaporization, and
heats of neutralization. Each will be considered separately.

Heats of Combustion.

These were determined in a Mahler bomb of about 300 cc.
content, in oxygen compressed to 25 atmospheres. The ar-
rangement and construction of the entire apparatus—with the
exception of the bomb itself—as well as the general method of
the experiments, was as nearly as possible that described by
Stohmann.[1]   The thermometer used was one of the Beckmann
type especially prepared for us by Goetze, in Leipzig, ac-
curately calibrated before use and compared to a normal ther-
mometer, which, in turn, had been tested against an air ther-
mometer.   The scale was divided into hundredths of a degree,
and by means of a strong magnifying glass provided with a
horizontal fiber in the eye-piece and so attached to the ther-
mometer stem that it could readily be slid up or down with-
out disturbing the horizontal position of the fiber, the estima-
tion of the thousandths could be made with a moderate degree
of certainty.

Since we had here to deal with extremely volatile substances
whose heats of combustion were to be determined in the liquid
state, it became necessary to devise an apparatus in which the
combustions, as well as the weighings, could be made with-
out any appreciable amount of vaporization taking place.
This was accomplished by the use of the crucible shown in
cross-section in the accompanying figure. The entire apparatus

[1] J. prakt. Chem., [2], **39**, 503 (1889).

is of platinum and consists of the crucible A, the upper part of
which is conical in shape, and a similarly con-
ical-shaped ring B, made of stout platinum
with an ear-piece at c, for handling. The
crucible and ring are ground to fit closely,
and by means of a brass form, into which the
crucible fits, and a plunger, the two can be
made to fit without difficulty and without
distortion. Thin films of denitrated cellulose were used
as covers, and, after the liquid was brought into the tared
crucible, the cellulose film, the weight of which had been
previously determined, was placed over it and the ring cen-
tered and pressed into place. If the film is not so thick
that the folds produced on pushing in the ring prevent the
latter from fitting the crucible closely, a very satisfactory
closure can be obtained, although a noticeable loss in weight
takes place at first until the film becomes saturated with the
vapors of the liquid, after which it decreases to a minimum,
rarely amounting to more than 0.0002 to 0.0003 gram per half
hour;[1] since the time required between the final weighing and
the beginning of the ensuing combustion rarely exceeded ten
minutes, the error produced from this cause is practically neg-
ligible. It was further demonstrated by repeated experi-
ments that in the compressed oxygen virtually no loss due to
evaporation of liquid ensued.
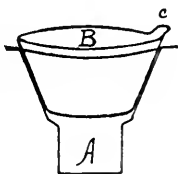
No difficulty was experienced in igniting the substance if
the coil of iron wire used as fuse be made to touch the cellu-
lose. Under these conditions the heated particles of the iron
oxide set fire at once both to the film and the substance, and
with this form of crucible the time required to communicate
the total heat to the water of the calorimeter, using 0.6 to 0.8
gram substance, was rarely more than three to four minutes.
Often a thin layer of unburned carbon from the film was
found at the end of the experiment between the collar and the
crucible; the weight of this was afterwards determined—it
varied usually between 0.0002 to 0.0008 gram—and brought

[1] α-Picoline seems to have a much more marked tendency to evaporate through
the film than any of the others. It will be observed in the tables which follow that
the heat values show a wider divergence from each other, probably because of this.

into the final correction, as was also the heat due to the combustion of the cellulose, the iron wire used for igniting, and the nitric acid formed by the burning of the nitrogen contained in the air originally in the bomb. The latter was absorbed in a measured quantity of water placed in the bottom of the bomb and determined by titration.

The water value of the solid parts of the apparatus was determined by burning weighed quantities of substances whose heats of combustion were accurately known.[1] For this purpose, carefully purified benzoic acid[2] and camphor[3] were made use of. These gave, as the mean of eight determinations, 389.1 grams ; the calculated value, using the weights and specific heats of the component parts was 389.2 grams. The agreement is of a very satisfactory character.

The weighed substance having been introduced into the bomb, and the latter filled with compressed oxygen, it was placed in the calorimeter, containing approximately 3 liters of water, the stirring apparatus set in motion, and the whole left for a time (about five minutes) to come to a uniform temperature. A number of readings of the thermometer were then taken from minute to minute until the rate of change had become uniform, when ignition was produced by means of an electric current from a storage battery. The subsequent rise in temperature is rapid, requiring rarely more than three to four minutes to attain the maximum, after which it slowly sinks. The temperature readings of the after-period were also taken from minute to minute until the change became constant, and the corrected temperature was then calculated according to the following equation :[4]

$$\Sigma \Delta t = \frac{v - v'}{\tau' - \tau}\left(\sum_{1}^{n-1} \theta r + \frac{\theta_n + \theta_1}{2} - n\tau\right) - (n-1)v.[5]$$

[1] Berthelot : Traité pratique de Calorimétrie Chimique, p. 145 ; and Stohmann : Ber. d. math.-phys. classe de Kgl. Säch. Gesell., (1893), p. 606.

[2] 6322.3 cal. Stohmann ; 6322.1 cal. Berthelot.

[3] 9291.6 cal. Stohmann ; 9288.0 cal. Berthelot.

[4] Stohmann, Kleber, and Langbein : *Loc. cit.*, p. 518.

[5] This formula differs slightly from the Regnault-Pfaundler correction formula (Pogg. Ann., **129**, 102) in that the value $\sum_{1}^{n-1} \theta r$ contains a special factor $\frac{\theta_2 - \theta_1}{9}$. This added factor has been determined experimentally by Stohmann and applies only to this type of apparatus. It is due to the fact that during the first minute of combustion about 94 per cent of the total heat given up is communicated to the calorimeter, and therefore the mean temperature change does not apply.

Here, n, n_1, and $n_2 =$ the number of observations taken during the combustion period, the fore-period, and the after-period, respectively.

τ_1, τ_2, τ_3 .... $\tau_{n_1} =$ the successive temperature readings during the fore-period from minute 1 to minute n_1.

τ'_1, τ'_2, τ'_3 .... $\tau'_{n_2} =$ the corresponding values during the after-period from minute 1 to minute n_2.

$v = \dfrac{\tau_{n_1} - \tau_1}{n_1 - 1} =$ the average change per minute during the fore-period.

$v' = \dfrac{\tau'_{n_2} - \tau'_1}{n_2 - 1} =$ the average change per minute during the after-period.

$\tau = \dfrac{\tau_1 + \tau_2 + \tau_3 + \cdots + \tau_{n_1}}{n_1} =$ average temperature of the fore-period.

$\tau' = \dfrac{\tau'_1 + \tau'_2 + \tau'_3 + \cdots + \tau'_{n_2}}{n_2} =$ average temperature of the after-period.

θ_1, θ_2, θ_3 .... $\theta_n =$ the temperature readings during the combustion, until the maximum is reached, and the temperature either remains constant or, as is more commonly the case, begins to fall.

$\sum_{1}^{n-1} \theta r = \theta_1 + \theta_2 + \theta_3 + \cdots + \theta_{n-1} + \dfrac{\theta_2 - \theta_1}{9} =$ observed rise during the combustion, increased by the experimentally determined factor $\dfrac{\theta_2 - \theta_1}{9}$ (see foot-note).

v in the above equation may be $\pm$ according to whether the temperature of the calorimeter has an upward or downward tendency; v' is constantly negative.

An example of the method of taking the readings and applying the formula will serve to make the matter clear. The thermometer readings are given in fractions of the scale divisions:

A liquid of unknown composition was burned; weight taken, 0.5479 gram.

Observations.

Fore-period.		Combustion.		After-period.	
τ_1	118.15	θ_1	118.80 (ignition)	τ'_1	289.25
τ_2	118.30	θ_2	258.00	τ'_2	288.95
τ_3	118.45	θ_3	286.00	τ'_3	288.80
τ_4	118.60	θ_4	289.10	τ'_4	288.65
τ_5	118.70	θ_5	289.35	τ'_5	288.40
τ_6	118.80	θ_6	289.25	τ'_6	288.25
				τ'_7	288.05
$n_1 = 6$		$n = 6$		$n_2 = 7$	

From which we deduce the following :

$$\tau = \frac{\tau_1 + \tau_2 + \cdots + \tau_6}{6} = 118.50.$$

$$\tau' = \frac{\tau'_1 + \tau'_2 + \cdots + \tau'_7}{7} = 288.62.$$

$$v = \frac{\tau_6 - \tau_1}{5} = +0.13.$$

$$v' = \frac{\tau'_7 - \tau'_1}{6} = -0.20.$$

$$\sum_1^{n-1} \theta r = \theta_1 + \theta_2 + \cdots + \theta_{n-1} + \frac{\theta_2 - \theta_1}{9} = 1256.72.$$

$$\frac{\theta_1 + \theta_n}{2} = 204.02.$$

Whence follows :

$$\Sigma \varDelta t = \frac{0.33}{170.12} (1256.72 + 204.02 - 711.00) - 0.65.$$

$$\Sigma \varDelta t = +0.80.$$

This correction then added to the final temperature reading of the period of combustion, *viz.*, 289.25, gives as the corrected maximum $\theta_n = 290.05$. The temperature at the beginning of the combustion is $\theta_1 = 118.80$. Hence the rise in temperature during the combustion, expressed in degrees, is :

$$\theta_n - \theta_1 = 1°.7125.$$

This increase is due not solely to the burning of the substance whose heat of combustion is to be determined, but a portion is caused by the burning of the cellulose film, the iron wire used as fuse, and the nitrogen in the bomb burned to

nitric acid. These, however, are factors which are either known or can be readily calculated, *e. g.* :

	Calories.
Heat given out, 1.7125 × 2900 (water value of the entire apparatus)	4966.25
To which is to be added for unburned carbon of the film,[1] 0.0035 gram × 8100.0 cal.	28.35
Total	4994.60

Heat due to :

	Calories.
Cellulose, 0.0147 gram × 4185.4	61.51
Iron wire, 0.0064 " × 1601.0	10.20
Nitric acid (by titration)	10.00
Total	81.71

$$4994.6 - 81.71 = 4912.89 \text{ cal.}$$

This amount of heat is produced by 0.5479 gram substance ; hence the heat of combustion per gram is :

$$4912.89 \div 0.5479 = 8966.77 \text{ cal.}$$

If the composition and the molecular weight of the substance is known, the molecular heat of combustion and the heat of combustion at constant pressure can be easily calculated from that at constant volume. These are given for each substance studied.

For convenience of reference the observations, together with the deduced heat values, have been tabulated, using for the purpose the original symbols of the Regnault-Pfaundler-Stohmann correction formula with the significations ascribed to them on page 10.

In nearly every case determinations have been made with different samples of substance, and in each instance before and after recrystallization, redistillation, etc. This furnishes a severe test for the purity of the substance, since the heat values are very sensitive to impurities, more so than the usual chemical tests, which, however, were also made use of. In each instance the substance used was thoroughly dried by standing several days over solid caustic potash, and distilled immediately before using.

[1] In the tables which follow, this correction has been applied to and reported in the value given for the cellulose, thus simplifying the correction.

Table I.—Pyridine.[1] C_5H_5N. 79.06.

			Number of determination.[2]			
	I.	II.	III.	IV.	V.	VI.
Amount of substance, gram.	0.5932	0.6264	0.9839	0.5909	0.5381	0.8537
v	0.09	0.10	0.10	0.29	0.20	0.21
v'	−0.23	−0.30	−0.66	−0.05	−0.09	−0.38
τ	49.63	55.80	213.90	62.19	32.70	34.42
τ'	221.29	235.91	505.90	236.12	192.41	315.21
$\sum_{1}^{n-1}\theta r$	712.73	768.04	2399.40	1247.38	806.01	887.09
n	5	5	7	7	6	5
$\dfrac{\theta_n + \theta_1}{2}$	135.8	146.3	360.80	149.60	112.97	158.75
$\sum \Delta t$	0.76	1.01	2.69	0.14	0.31	1.00
θ_n (corr.), degrees	2.2251	2.3761	5.0896	2.3639	1.9316	2.8365
θ	0.4985	0.5600	2.1381	0.6295	0.3310	0.3485
$(\theta_n - \theta_1)$. 2911.6[3] cal.	5027.17	5287.76	8264.20	5029.76	4641.74	7215.20
Correction for Fe, cal.	10.2	10.2	9.1	10.3	10.3	10.3
" HNO₃, cal.	13.5	16.0	10.6	14.0	12.5	19.0
" cellulose, cal.	61.26	37.36	40.4	80.68	137.99	78.03

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8331.4	658.4	99.96
II.	8340.0	659.4	100.09
III.	8338.3	659.2	100.07

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
IV.	8334.4	658.9	100.02
V.	8327.4	658.4	99.93
VI.	8326.0	658.3	99.92
Mean,	8332.9		

658.8 for constant volume } at 15°
659.2   "   " pressure }
−16.7 heat of formation

[1] In the table all temperature values—unless otherwise stated—are expressed in fractional parts of the Beckmann scale divisions.
[2] Nos. V. and VI. were made with a specially purified sample received from Kahlbaum.
[3] In No. III. the water value was 2800, in Nos. IV., V., and VI. it was 2900.

Table II.—α-Picoline. C_6H_7N. 93.11.[1]

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
				Number of determination.[1]				
Amt. of subst., gram.	0.6693	0.6328	0.6529	0.6273	0.6258	0.5872	0.6115	0.5969
v	0.23	0.20	0.26	0.19	0.20	0.21	0.15	0.23
v'	—0.21	—0.20	—0.21	—0.20	—0.18	—0.13	—0.19	—0.13
τ	122.05	118.62	112.36	124.37	106.30	98.61	150.23	93.12
τ'	324.34	310.31	310.36	316.60	298.73	279.27	337.01	276.05
$\sum_{1}^{n-1}\theta r$	1101.47	1053.08	1051.04	1393.74	1300.07	1210.96	1497.44	1191.59
n	5	5	5	6	6	6	6	6
$\dfrac{\theta_n+\theta_1}{2}$	223.72	214.97	211.97	221.03	203.00	189.28	244.08	185.08
$\sum \Delta t$	0.63	0.61	0.62	0.81	0.71	0.45	0.78	0.91
θ_n (corr.), degrees	3.2548	3.1141	3.1157	3.1791	2.9991	2.7995	3.3833	2.7731
θ "	1.2260	1.1915	1.1300	1.2495	1.0680	0.9905	1.5060	0.9375
$(\theta_n - \theta_1). 2911.6^2$ cal.	5907.05	5597.84	5781.56	5595.84	5580.88	5246.10	5444.17	5323.24
Correction for Fe.	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2
" HNO_3	16.0	15.0	15.5	15.0	13.5	14.5	12.0	14.0
" cellu-lose	28.91	33.51	28.07	72.60	67.02	71.99	75.07	84.37

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.	No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8743.4	814.1	99.84	V.	8773.0	816.9	100.18
II.	8753.3	815.0	99.96	VI.	8769.4	816.5	100.14
III.	8772.8	816.8	100.18	VII.	8744.0	814.2	99.85
IV.	8764.6	816.1	100.08	VIII.	8736.3	813.5	99.76
				Mean,	8757.1		

815.4 for constant volume } at 15°
816.1 " pressure }
—10.6 heat of formation

[1] Nos. IV. to VIII. represent a second sample of the base.
[2] The water value in Nos. IV., VI., VII., and VIII. was taken at 2900, in No. V. at 2890.

Table III.—β-Picoline. C_6H_7N.   93.11.

	Number of determination.[1]				
	I.	II.	III.	IV.	V.
Amt. of substance, gram.	0.5034	0.6449	0.6375	0.6295	0.5624
v	0.13	0.24	0.20	0.24	0.17
v'	—0.17	—0.13	—0.17	—0.20	—0.22
τ	85.63	89.58	89.75	90.30	159.40
τ'	238.07	284.70	283.18	280.59	330.72
$\sum_{1}^{n-1}\theta r$	1042.42	946.66	942.70	1219.26	1487.24
n	6	5	5	6	6
$\dfrac{\theta_n + \theta_1}{2}$	162.23	187.58	186.90	186.00	245.65
$\Sigma\,\Delta t$	0.71	0.34	0.47	0.79	0.92
θ_n (corr.), degrees	2.3921	2.8534	2.8407	2.8189	3.3222
θ_1 "	0.8595	0.9015	0.9020	0.9090	1.6000
$(\theta_n — \theta_1)$. 2911.6² cal.	4462.32	5683.15	5644.72	5560.86	4994.38
Correction for Fe, cal.	10.2	10.2	10.2	10.2	10.2
" HNO₃, cal.	12.0	14.5	16.5	16.0	12.5
" cellulose, cal.	50.75	34.58	46.99	44.06	66.34

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8719.4	811.9	99.94
II.	8720.5	812.0	99.95
III.	8738.9	813.7	100.17

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
IV.	8722.2	812.2	99.97
V.	8722.2	812.2	99.97
Mean,	8724.6		

812.4 for constant volume } at 15°
813.1 "   pressure }
—7.6 heat of formation

---

[1] No. V. was made with a second sample of β-picoline.   [2] The water value used in No. V. was 2900.

Table IV.—γ-Picoline. C_6H_7N. 93.11.

	I.	Number of determinations. II.	III.
Amt. of substance, gram.	0.6495	0.6712	0.5675
v	0.24	0.33	0.24
v'	—0.15	—0.12	—0.12
τ	116.43	81.99	108.53
τ'	316.22	288.82	282.58
$\sum_{1}^{n-1} \theta r$	1070.73	1244.73	1244.49
n	5	6	6
$\dfrac{\theta_n + \theta_1}{2}$	216.92	186.05	195.95
$\sum \varDelta t$	0.43	0.40	0.43
θ_n (corr.), degrees	3.1713	2.8955	2.8333
θ_1 "	1.1715	0.8295	1.0900
$(\theta_n - \theta_1)$, 2900 cal.	5799.42	5991.40	5055.57
Correction for Fe, cal.	10.2	10.2	10.2
" " HNO_3, cal.	14.5	17.0	14.5
" " cellulose, cal.	82.34	85.50	54.06

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8764.3	816.0	100.00
II.	8758.5	815.5	99.94
III.	8769.7	816.6	100.07
Mean,	8764.2	816.0 for constant volume ⎱ at 15°	
		816.7 " " pressure ⎰	
		—11.2 heat of formation	

Of the pyridine bases, so far as known to us, the heat of combustion of one only, pyridine, has been previously determined. This has been done by Thomsen,[1] using pyridine vapor, and by Delépine,[2] who determined it for the liquid. The former gives the value 675.1 Cal. for the vapor at 18° C., while Delépine gives 665.1 Cal. for the liquid, from which he calculated the value 673.7 Cal. for the vapor. The numbers obtained by us, *viz.*, 659.2 Cal. for the liquid and 667.6 Cal. for the vapor— the latter calculated from the former by addition of the molecular heat of evaporation (see p. 31)—are somewhat lower

[1] Thermochem. Untersuch., **4**, 144.
[2] Compt. rend., **126**, 1794 (1898).

than those given by these two observers.   We feel inclined to consider our values as more nearly correct, great pains having been taken to have a pure product for the purpose of these experiments.   They are, moreover, when considered in conjunction with the corresponding values obtained from the higher homologues, more nearly in accord with the previously observed rule for the increase in thermal value in an homologous series.   On account of the lack of detailed information, especially as regards methods of purification, we find it impossible to criticise the results obtained by these investigators more nearly.   The fact that commercial pyridine, unless very carefully purified, is almost sure to contain traces of higher homologues, suggests the possibility of the higher results being due to this cause.

An examination of the tabulated values shows that certain regularities exist for the pyridine bases which are closely in accord with those observed for other homologous series.   It will be seen, for instance, upon considering the following table, that a constant ratio holds between pyridine and its higher homologues, *viz.* :

	Heat per gram-mol., Cal.	Difference from pyridine, Cal.
Pyridine, C_5H_5N	659.2	. . . .
α-Picoline, C_6H_7N	816.1	156.9
β-Picoline, C_6H_7N	813.1	153.9
γ-Picoline, C_6H_7N	816.7	157.5
		Mean, 156.1

This constant is approximately 156 Cal.   The same value has been found by other observers, notably by Stohmann and his pupils, who have established it as a general rule, based upon a large number of observations upon homologous compounds in both the fatty and aromatic series.   The relation may be formulated thus :

$$X = -H + CH_3 + 156 \text{ Cal.}[1]$$

Or, in words, the change in the heat of combustion due to the addition or subtraction of $CH_2 = \pm 156$ Cal.

[1] Stohmann : J. prakt. Chem., [2], **35,** 41 (1887).

The time at our disposal has not been sufficient for the preparation and examination of other of the higher homologues of the series, but we have obtained as the result of a single determination, made with a very small quantity of lutidine, the mercury salt of which was obtained as a by-product during the preparation of γ-picoline, the following heat values :

	Per gram-mol.	
Per gram. cal.	Constant volume. Cal.	Constant pressure. Cal.
9037.2	967.9	968.9

This gives as the average difference from the picolines, due to CH_2, the value 154 Cal., thus indicating the constancy of the ratio for the entire pyridine series.

We hope later, by examining the higher homologues of this series, to be able to bring further evidence in support of this, but consider it possible to establish from the above a formula which permits an approximate calculation of the heats of combustion of the pyridine compounds from their empiric formula, thus :

$$C_nH_{2n-5}N = 659.2 \text{ Cal.} + (n-5) \; 156 \text{ Cal.}[1]$$

In support of this we give the following calculated and observed values :

Substance.	Heats of combustion at constant pressure.	
	Calculated. Cal.	Observed. Cal.
Pyridine	659.2	659.2
Picoline	815.2	815.3 (average of the three picolines)
Lutidine	971.2	968.9

On comparing the heats of combustion of the picolines with that of the metameric compound, aniline, determined by Petit,[2] it will be observed that another rule which has been established for the fatty and aromatic series is also valid for the pyridine compounds, *viz.*, that isomers possess practically the same heats of combustion, whereas metamers have a higher value,[3] thus :

[1] For analogous formulæ for aliphatic hydrocarbons see Berthelot and Matignon : Compt. rend., **116**, 1333 (1893).

[2] *Ibid.*, **106**, 1089.

[3] Ostwald : Grundriss der allgemeinen Chemie.

Substance.	Heat per gram. cal.	Heat per gram-mol. Constant volume. Cal.	Heat per gram-mol. Constant pressure. Cal.
α-Picoline	8757.1	815.4	816.1
β- "	8724.6	812.4	813.1
γ- "	8764.2	816.0	816.7
Aniline	8794.0	817.8	818.5

For comparison may be cited the respective data for the isomeric cresols[1] and their metamer, anisol :[2]

Substance.	Per gram, cal.	Per gram-mol. Constant pressure. Cal.
o-Cresol	8176.0	883.0
m- "	8157.0	881.0
p- "	8175.0	882.9
Anisol	8345.0	901.3

The values just given serve to bring out more clearly another point to which we wish to call attention, *viz.*, that in the case of isomers the position of the substituting group seems to produce a greater effect upon the energy content in the case of the meta than with the ortho and para compounds, for in both of the cases cited the heats of combustion of the ortho and para compounds are practically identical, while that of the meta compound is slightly lower.

An examination of the published data with the idea of determining the general character of this led to no very satisfactory conclusion, the data not being sufficient for the purpose, while some of that given is old and possibly in need of revision. The indications are that, in general, the meta compounds exhibit a variation from the ortho and para, being sometimes higher, occasionally agreeing, but more often giving lower values.[3]

Heats of Formation.

These have been tabulated above in conjunction with the heats of combustion (p. 14), from which they were obtained by first calculating the heats of combustion of the composing elements, using for this purpose the values $C = 94$ Cal., $H_2 = 69$

[1] Stohmann, Rodatz, and Herzberg : J. prakt. Chem., [2], **34**, 312.
[2] *Ibid.*, **35**, 23.
[3] Stohmann : Ztschr. phys. Chem., **6**, 334 ff ; **10**, 410 ff.

Cal.[1] (since the nitrogen contained in the substance is not burned, but liberated in the elementary state, it is not here taken into consideration), and then subtracting from the sum thus obtained the heat of combustion of the corresponding compound, which gives as difference the heat of formation of the latter.

It has been shown above that the increase in the heat of combustion in the pyridine series, for each CH_2, is equal to 156 Cal. This enables us to calculate for this series the heat of formation of the CH_2 group, *viz.* :

$$C + O_2 = CO_2 + 94 \text{ Cal. ;}$$
$$H_2 + O = H_2O + 69 \text{ Cal.}$$

Therefore,

$$C + H_2 + O_3 = CO_2 + H_2O + 163 \text{ Cal.}$$
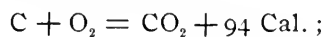
for the elements, while

$$CH_2 + O_3 = CO_2 + H_2O + 156 \text{ Cal.}$$
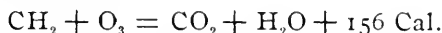
for the compound, which gives :

$$C + H_2 = CH_2 + 7 \text{ Cal.,}$$

the heat of formation of CH_2, and this furnishes a general formula for the calculation of the heats of formation of pyridine and its homologues, *viz.* :

$$C_nH_{2n-5}N = -51.7 \text{ Cal.} + n.7 \text{ Cal.}$$
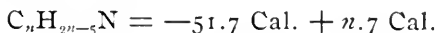
Specific Heats.

In his classical work upon the specific heats in homologous series of liquid organic compounds,[2] Schiff was able to show, as the result of an extraordinarily painstaking series of experiments upon a very large number of compounds, that the variation of the specific heat of a substance with the temperature is expressed by a very simple formula, *viz.*, that of a straight line; and further, that for an homologous series this variation is of a uniform nature, the same expression serving for all the members of the series, or they can be represented by a small number of parallel straight lines.

This, as well as certain other generalities contained in that

[1] Stohmann : Ztschr. phys. Chem., **6**, 334.
[2] Ann. Chem. (Liebig), 234, 300 (1886).

article, induced us to undertake an investigation of the specific
heats of the compounds of the pyridine series with the idea of
determining to what degree the relations established by that
author are general in character, or at least to determine
whether this regularity extends to this series.

As a preliminary to the discussion of our results, which
can best be done after the results themselves have been given,
we may state that they are not entirely in accord with the
laws deduced by Schiff, although the divergence is of
such a character that, considering the difficulty of establish-
ing a generalization from a small number of observations, it
is not improbable that the accordance is, nevertheless, of a fairly
satisfactory character.   In carrying out work of this nature,
it is necessary, in order to attain a satisfactory degree of accu-
racy, to consider and eliminate as far as possible, the various
conditions operating against the accuracy of the method.
Schiff has already called attention to some of these,[1] the chief
of which are the condition of purity of the material used and the
possible error attached to the Berthelot form of apparatus, due
to the immersion of the enclosed thermometer along with the
container of the liquid during the cooling of the latter.   Re-
garding the condition of purity of our substances, we have
already spoken under the description of the methods of puri-
fication and the determination of the heats of combustion.
The latter source of error was avoided by the use of the Schiff
form of apparatus,[2] consisting of a platinum vessel made in
the form of a cross, which acts admirably as a stirrer, and
provided with a short, wide, thin-walled glass tube inserted
tightly by means of a cork, which was also used as a handle
in stirring. The thermometer was inserted loosely through this,
by means of a cork, and dipped into the liquid below ; before
bringing the vessel into the calorimeter, the thermometer was
removed and a small calcium chloride tube inserted to prevent
the absorption of moisture.   Any uncertainty caused by
variation in the amount of heat given up by the thermometer
was thus obviated.

In addition to the above-mentioned sources of error there

[1] *Loc. cit.*, 302.
[2] *Loc. cit.*, 303, with cut of apparatus.

are two others which should be considered, first, a part of the substance exists at the time of immersion into the calorimeter in the form of vapor, a portion of which, corresponding to the difference between the vapor pressures at the higher and the lower temperatures is condensed to liquid, so that there is included in the heat given off the heat of evaporation of this portion of the liquid, thus giving rise to too high a result. The second source of error is that due to the unknown loss of heat in transferring the platinum vessel from the heating apparatus to the calorimeter. This loss was reduced to a minimum by having the heating apparatus placed relatively near the calorimeter, the latter naturally being carefully shielded from radiated heat, and in such a position that the transfer could be made in the least possible time, never more than a fraction of a second being required. We have sought to reduce the first-mentioned source of error to a minimum by never heating the liquid more than to within 10° of its boiling-point. The two sources of error have a tendency to counteract each other, which lessens, to some degree, the absolute error of the method. The agreement in Schiff's results as well as in our own shows that the error thus introduced is of a negligible character.

The liquid, whose specific heat was to be determined, was heated by means of the vapors of a suitable liquid to the desired temperature. For heating liquids we used acetone, alcohol, water, toluene, and mixtures of toluene and xylene. The temperature of the liquid to be studied was taken by means of an immersed thermometer, being further controlled by surrounding the projecting stem with a wide glass tube whose upper end was closed by a cork and containing a second thermometer so placed that the medium temperature of the mercury thread outside the flask could be determined and the necessary correction made. The readings were taken by means of a cathetometer telescope and could be made with accuracy to hundredths of a degree. The immersion of the platinum flask into the water of the calorimeter did not take place until the liquid had shown a constant temperature for fifteen to twenty minutes.

As calorimeter thermometer we used an instrument constructed by the well-known instrument-maker, Golaz, in Paris; this was divided into $0°.02$, and the readings were estimated to the thousandths by means of a strong lens. The thermometer calibration was controlled by comparison with a normal instrument, the comparison having been made a short time before using.

The calorimeter vessel was of such size that with 500 cc. water the platinum cross was immersed to just below the cork. The weight of the liquid taken was usually 40-50 grams, determined at the end of each experiment and corrected—as was that of the water in the calorimeter—for density, the corrected values being used in the calculations.

As unit of heat, we used the so-called *15° water-calorie*, defined as that quantity of heat required to raise the temperature of 1 gram water from $14°.5$ to $15°.5$, measured in terms of the hydrogen thermometer.[1] For purposes of calculation we have availed ourselves of the determinations made on the specific heat of water between $0°$ and $100°$ by Lüdin,[2] and have, for purposes of extrapolation, used the formula given by him, *viz.*:

$$C_{T,\theta} = 1 + \frac{\alpha}{2} (T + \theta) + \frac{\beta}{3} (T^2 + T\theta + \theta^2) +$$
$$\frac{\gamma}{4} (T^3 + T^2\theta + T\theta^2 + \theta^3) \; ; \text{ where}$$

C = medium specific heat of water between the temperatures $T°$ and $\theta°$.

$$\frac{\alpha}{2} = - 0.000271396.$$

$$\frac{\beta}{3} = + 0.00000484567.$$

$$\frac{\gamma}{4} = - 0.0000000021214.$$

The value thus obtained, divided by $C_{15} = 0.9949$,[3] gives the desired mean specific heat between T and θ.

[1] Warburg : Referat über die Wärmeeinheit, Leipzig (1900), p. 13; Kohlrausch, Lehrbuch der prakt. Physik., 9th ed. (1900), p. 179.

[2] Die Abhängigkeit der specif. Wärme des Wassers vou der Temperatur—Mitteilung der naturwiss. Gesell. Winterthur, Heft II (1900) ; also Warburg: *Loc cit.*, p. 14.

[3] The true specific heat of water at $15°$, $C_0 = 1$.

The thermometer readings were corrected by means of the Regnault-Pfaundler formula,[1] and the specific heat values calculated according to the following equation :

$$\Delta T[(G \times x) + (w \times s)] = \Delta\theta(W \times s'),$$

which gives, on solving for x,

$$x = \frac{\Delta\theta(W \times s') - w \times s}{G\Delta T}.$$

Here :

$x =$ specific heat of the liquid between $T°$ and $\theta°$.

$s =$ specific heat of water between $T°$ and $\theta°$.

$s' =$ specific heat of water between $15°$ and $\theta°$.

$T =$ temperature of the liquid at the moment of immersion.

$\theta =$ (corr.) end temperature of the water (also of the liquid.

$t =$ temperature of the water at the moment of immersion.

$\Delta T = T° - \theta° =$ (corr.) temperature change in the liquid.

$\Delta\theta = \theta° - t° =$ (corr.) temperature change in the water.

$G =$ (corr.) weight in grams of liquid used.

$w =$ water value of the platinum vessel.

$W =$ total water value of the calorimeter (water + container + thermometer).

The symbols have the same significance in the tables on the next page.

An examination of the values given shows that between the same range of temperatures the specific heats of α- and β-picoline are practically identical and can be expressed by the equation

$$C_{T-\theta} = a + b(T + \theta)$$

for the mean specific heats, in which a has the value 0.3848 and b the value 0.000387, *i. e.*,

$$C_{T-\theta} = 0.3848 + 0.000387(T + \theta).$$

For the true specific heat the equation becomes

$$C_t = a + 2bt,$$

Pogg. Ann., **129**, 102.

Table V.—Pyridine.

No.	G.	w.	w.	s.	s.	T.	θ.	l.	ΔT.	Δθ.	x.	Mean.
1	54.4068	517.953	2.7677	1.0061	0.9997	54.60	16.2611	14.4100	38.3389	1.8511	0.4083	0.4084
2	54.3862	"	"	"	"	54.65	16.4830	14.6400	38.1670	1.8430	0.4085	
3	54.4682	"	"	"	"	76.47	17.4332	14.5420	59.0368	2.8912	0.4144	0.41445
4	54.4342	"	2.7686	"	"	76.47	17.9277	15.0620	58.5423	2.8657	0.4145	
5	50.3644	"	"	"	"	98.22	20.6820	17.0900	77.5380	3.5920	0.4209	0.4201
6	50.3000	"	"	"	"	98.31	21.5440	17.9990	76.7660	3.5450	0.4193	

α-Picoline.

No.	G.	w.	w.	s.	s.	T.	θ.	l.	ΔT.	Δθ.	x.	Mean.
1	46.3457	517.953	2.7676	1.0061	0.9997	76.80	19.0593	16.5700	57.7407	2.4893	0.4216	0.42195
2	46.3259	"	"	"	"	76.81	19.2434	16.7590	57.5666	2.4844	0.4223	
3	46.4559	"	"	"	"	98.41	19.5505	16.0820	78.8595	3.4685	0.4303	0.4295
4	46.3893	"	"	1.0066	"	98.32	20.0952	16.6700	78.2248	3.4252	0.4287	
5	46.1739	"	"	"	"	108.71	18.8932	14.9280	89.8168	3.9652	0.4347	0.43465
6	46.1035	"	"	"	"	108.82	19.4389	15.5010	89.3811	3.9379	0.4346	
7	46.1973	"	"	"	"	118.10	21.8279	17.5400	96.2721	4.2879	0.4386	0.43895
8	46.1045	"	"	"	"	118.47	19.4806	15.0760	98.9892	4.4046	0.4393	

β-Picoline.

No.	G.	w.	w.	s.	s.	T.	θ.	l.	ΔT.	Δθ.	x.	Mean.
1	45.6799	517.953	2.7676	1.0061	0.9997	76.62	17.9893	15.4800	58.6307	2.5093	0.4242	0.4245
2	45.6608	"	"	"	"	76.67	18.3588	15.8620	58.3112	2.4968	0.4248	
3	45.6033	"	"	"	"	96.41	19.9750	16.6670	76.4350	3.3080	0.4303	0.4299
4	45.5827	"	"	1.0066	"	96.88	19.8331	16.5060	77.0470	3.3271	0.4294	
5	45.9110	"	"	"	"	121.83	19.7478	15.2560	102.0822	4.4918	0.4356	0.43565
6	45.8352	"	"	"	"	121.51	19.9381	15.4740	101.5719	4.4641	0.4357	
7	45.7522	"	"	"	"	129.71	20.5142	15.6800	109.1958	4.8342	0.4402	0.4414
8	45.7085	"	"	"	"	129.39	20.7720	15.9480	108.618	4.8240	0.4427	

or, substituting the values of a and b given above,

$$C_t = 0.3848 + 0.000774t.$$

For pyridine the equations are:

$$C_{T-\theta} = 0.3915 + 0.000242(T + \theta);$$

and

$$C_t = 0.3915 + 0.000484t.$$

A comparison of the values found with those calculated establishes the correctness of the above formulas, *viz.* :

Table VI.—*Pyridine.*

No.	T.	θ.	Specific heat. Found.	Calculated.
1	54.60	16.26	0.4083	0.4086
2	54.65	16.48	0.4085	0.4087
3	76.47	17.43	0.4144	0.4142
4	76.47	17.93	0.4145	0.4144
5	98.22	20.68	0.4209	0.4196
6	98.31	21.54	0.4193	0.4198

α-Picoline.

No.	T.	θ.	Found.	Calculated.
1	76.80	19.06	0.4216	0.4219
2	76.81	19.24	0.4223	0.4220
3	98.42	19.55	0.4302	0.4304
4	98.32	20.09	0.4287	0.4306
5	108.71	18.89	0.4347	0.4342
6	108.82	19.44	0.4346	0.4345
7	118.10	21.83	0.4386	0.4389
8	118.47	19.48	0.4393	0.4382

β-Picoline.

No.	T.	θ.	Found.	Calculated.
1	76.62	17.99	0.4242	0.4214
2	76.67	18.36	0.4248	0.4216
3	96.41	19.97	0.4303	0.4298
4	96.88	19.83	0.4294	0.4300
5	121.83	19.75	0.4356	0.4394
6	121.51	19.94	0.4357	0.4395
7	129.71	20.51	0.4402	0.4429
8	129.39	20.77	0.4427	0.4429

We were unable to establish for this series the correctness of Schiff's rule, that in homologous series the curves expressing the change of specific heat with the temperature are represented by a series of parallel straight lines (when not by

the same line). A glance at the temperature factor for pyridine and the picolines shows that for this series, as far as it applies to the two homologues considered, the lines are not parallel, but slightly divergent, as is shown by the following curves. In Table A are represented the mean specific heats as actually found, for the temperatures given, while in Table B are shown the specific heats calculated from the formulas given above and reckoned for the same ranges of temperature for pyridine and for the picolines. The temperatures used in the calculation were selected arbitrarily, but as far as possible with the idea of keeping closely within range of the temperature intervals used in the actual observations.

The specific heat of pyridine has been previously determined by Colson,[1] Delépine,[2] and by Kahlenberg.[3] None of these find a value entirely in accord with that obtained by us. Colson gives 0.412 between 34°.65 and 14°.07 ; Delépine gives 0.4241 between 98° and 16°, while Kahlenberg finds 0.4313 between 108° and 21°. It is difficult to estimate the relative value of these ; Colson states that he did not aim at a very great exactitude ; Delépine gives too little data to enable us to determine the actual conditions under which he operated. Kahlenberg's value appears to us to be too high, though as it is likely that his unit for the calorie was different from that used by us, we are unable, for lack of the necessary data, to make a comparison of the two values by recalculating his results. Since that author also made use of the Berthelot form of apparatus, the disadvantages of which Schiff has already called attention to,[4] it is not improbable that this may have influenced his results to some extent.

Kahlenberg has also determined the specific heat of α-picoline[5] as 0.4342 between 124° and 22°. This value, which is somewhat lower than ours, may also be found more nearly in accord with it upon recalculating to the same units.

It is evident that, in general, in the determination of the

[1] Ann. chim. phys., [6], **19**, 409 (1890).

[2] Compt. rend., **126**, 1794 (1898).

[3] J. Phys. Chem., **5**, 229 (1901).

   Ann. Chem. (Liebig), **234**, 304.

[5] *Loc. cit.*, p. 284.

specific heats of liquids, too little attention has heretofore been paid to the proper purification of the substances used. Schiff has called attention to this,[1] and our experience fully supports his statement that the slightest trace of impurity produces a very marked influence upon the specific heat.

Heats of Evaporation.

For the purpose of determining the latent heats of evaporation of the substances under investigation, we made use of the apparatus of Schiff,[2] constructed entirely of platinum. Kahlenberg, in an article bearing upon this subject,[3] raises an objection to this form of apparatus, stating that in the case of liquids with high boiling-points the liquid condenses in the trap and eventually some of it runs over into the condenser. Our results do not bear out this objection, for, although working with moderately high-boiling liquids, we failed to note a single instance in which this happened. It is probable that Kahlenberg's tests were made with a glass trap, which, on account of the relatively high specific heat of glass, might require a considerable amount of liquid to be condensed in the trap before the inner tube assumed the temperature of the vapor, especially so if the tube leading from the boiling vessel to the trap was not sufficiently wide or the heating too rapid to permit the condensed liquid to run back into the retort. With a wide tube of metal, such as silver or platinum, and a proper regulation of the rate of boiling, this would not be the case, as the results given by Schiff who used a silver tube, and those to be presented by us, when a tube of platinum was used, most definitely prove. An entire apparatus of metal naturally possesses another advantage in that it gives up its heat much more readily than one of glass, and can be used for all forms of liquids, some of which attack glass.

The operation was carried out under conditions similar to those described under specific heats, using a similar form of calorimeter and thermometer. The calorimeter vessel was of such size that the condenser was immersed to a point just be-

[1] *Loc. cit.*, p. 307.
[2] Ann. Chem. (Liebig), **234**, 338 (1886).
[3] J. Phys. Chem., **5**, 217 (1901).

neath the cork, and the water and thermometer were carefully
protected from influences of radiation, which can be more
conveniently done with this form of apparatus than with the
upright heater of Berthelot or that described by Kahlenberg.[1]

The apparatus was thoroughly tested by using liquids
whose latent heats of evaporation are known. In every case
from 20 to 30 grams of substance were condensed, which re-
quired four to six minutes, the boiling being so regulated
that the thermometer rose only about one degree per minute,
the total rise in the calorimeter being usually 4° to 5°. The
15°-calorie was used as the unit in making the calculations,
and all weighings were corrected for the specific gravity of
the liquid.

The latent heats of vaporization of pyridine and of α-pico-
line have already been determined by Kahlenberg.[2] Our re-
sults upon the specific heats of these liquids, however, differ-
ing so markedly from his, and furthermore, as has been shown
above, the specific heat varying with the temperature, it was
thought best to repeat his determinations of the heats of
evaporation of these substances, using the extrapolated values
for the specific heats at the boiling-point of the liquid in ques-
tion, making use of the equation given on page 24 for this
purpose. From this the mean specific heat between the boil-
ing-point and the end temperature could be obtained and in-
serted in the calculations.

The formula used was

$$H = \frac{W(\Delta\theta \times s) - G(\Delta T \times \delta)}{G},$$

in which, and for the following tables:

B_o = barometric reading, reduced to 0°.

T = boiling-point of the liquid.

G = weight of liquid condensed.

W = total water value of the apparatus (water + water
value of the solid parts).

s = specific heat of water between 15° and $\theta°$.

δ = specific heat of the liquid between $T°$ and $\theta°$.

[1] *Loc. cit.,* p. 221.
[2] *Loc. cit.*

$\theta =$ end temperature in the calorimeter.

$t =$ original temperature of the water.

$\Delta T = T° - \theta° =$ (corr.) temperature change in the liquid.

$\Delta\theta = \theta° - t° =$ (corr.) temperature change in the water.

$H =$ latent heat of evaporation per gram substance, expressed in $15°$-calories.

From the data contained in the table the values found for the Trouton constant,[1] $\dfrac{MH}{T} = C$, are : For pyridine, 21.9 ; α-picoline, 21.5 ; β-picoline, 21.3, the mean of which is 21.6. This value approaches closely to that found by Schiff for a large number of the esters of the fatty series and also certain of the aromatic hydrocarbons. Schiff's number is 20.8.[2] It appears evident, therefore, that in the pyridine series also, the molecular heats are proportional to the absolute temperatures at which evaporation takes place.

In order to obtain the normal heats of evaporation, *viz.*, those which correspond to the boiling-points under normal pressure—this constituting in reality the only condition under which a true comparison of these can be made—we have, using the mean 21.6, deduced these to be :

	Calories.
Pyridine	106.1
α-Picoline	93.3
β- "	96.7

Kahlenberg's value for pyridine, 104.0,[3] recalculated to normal conditions, yields as the normal heat of evaporation 104.3. His number for α-picoline, 90.75,[4] gives in the same way as the normal heat of evaporation, 90.9. Considering the differences in method, and more particularly in the specific heats used, this must be pronounced a fairly satisfactory agreement.

It was further of interest to calculate for these substances the constant expressing the molecular rise of boiling-point, especially since pyridine, and possibly also α-picoline, seem well suited as solvents for molecular weight determinations.

[1] Phil. Mag., [5], **18**, 54 (1884) ; Beiblätter, **8**, 643.

[2] Ann. Chem. (Liebig), **234**, 348 (1886) ; Ostwald : Lehrbuch der allgemeinen Chemie, 2te Aufl., **1**, 354.

[3] *Loc. cit.*, p. 230.

[4] *Loc. cit.*, p. 286.

Constam and White.

Table VII.

No.	Substance.	B₀. mm.	T.	G.	W.	s.	δ.	θ.	i.	ΔT.	Δθ.	H.	Mean.
1	Pyridine	715.9	113.55	29.0457	980.06	0.9997	0.4238	20.0528	15.700	93.4972	4.3528	107.2	107.33
2	"	720.2	113.71	29.1172	"	"	0.4234	19.5785	15.206	94.1315	4.3725	107.3	
3	"	719.1	113.67	30.9310	"	"	0.4238	19.9310	15.280	93.7390	4.6510	107.6	
4	α-Picoline	727.8	127.73	30.8353	"	"	0.4417	19.3363	14.9140	108.3937	4.4223	92.65	92.7
5	"	727.8	127.73	26.2262	"	"	0.4415	18.7726	15.0020	108.9574	3.7706	92.76	
6	β-	723.3	141.73	24.1747	"	"	0.4473	19.7723	16.1040	121.9577	3.6683	94.12	94.82
7	"	720.9	141.64	21.2152	"	"	0.4471	19.4047	16.1680	122.2353	3.2367	95.52	

The calculation was made by inserting the normal heats of evaporation in the Arrhenius-Beckmann formula, $K = \dfrac{0.02T.^2}{H}$ The numbers found for K are :

$$\text{Pyridine, } K = 28.4 ;$$
$$\alpha\text{-Picoline, } K = 34.6 ;$$
$$\beta\text{-} \quad \text{``} \quad K = 35.8.$$

From the values obtained by him, Kahlenberg calculated the boiling-point constant, K, for pyridine 28.8, and for α-picoline 35.6. Werner obtained by direct observation of the increase in the boiling-point, using pyridine as a solvent, K for pyridine $= 30.07$. The latter made no particular point, however, of using absolutely pure substance or of attaining great accuracy in the results.

Heats of Neutralization.

Although it is generally known that the heats of neutralization do not serve as an absolute measure of the affinities of acids or bases, we nevertheless undertook to determine the respective data for pyridine and for two of the picolines in order to ascertain whether the comparative values thus obtained follow the same order as their affinity-constants determined by us electrolytically.

For this purpose we availed ourselves of the excellent and simple form of apparatus described by Thomsen,[1] with the single modification that the upper vessel was of glass. This, however, was carefully protected from heat radiation, being surrounded with a thick layer of felt with an air space between the two, and further, by a polished metal cylinder covered with a plate of hard rubber, which did not touch the inside vessel. The temperature of the room during the whole investigation was kept between 17° and 18° C.[2] The thermometers used were of the type described under specific heats and had previously been compared with each other throughout their entire ranges of temperature.

The observed differences in temperature between the acid

[1] Thermochem. Untersuch., I, 19.
[2] Thomsen : *Loc. cit.*, p. 59.

and alkali before mixing were very slight, amounting to only a few tenths of a degree.

For the neutralization equal quantities (300 cc.) of exactly $N/2$ hydrochloric acid and $N/2$ solution of the base were used, the solutions being made in specially prepared "conductivity" water, freed as far as possible from carbon dioxide and ammonia. The solution of the base was prepared by weight, using the thoroughly dried and recently distilled base, the weighings being made in a specially constructed vessel which closed perfectly and from which, without exposure to the air, the liquid could be run directly into water contained in an accurately calibrated measuring-flask. All volumes were taken at $17°.5$ C.

In order to determine the amount of acid actually consumed and likewise of base neutralized, the acid container—the upper vessel—was rinsed out at the end of the experiment and the unused acid titrated with $N/10$ barium hydroxide solution. The amount thus obtained was deducted from the total taken (300 cc.) and the corrected value introduced in the final calculation.

The time required, after mixing, to attain the maximum was never more than one minute. The calculations were made by means of Berthelot's formula,[1] assuming the weights and specific heats of the liquids to be the same as those of water. This is not absolutely the case, but as both Thomsen[2] and Berthelot[3] have proved, the error thus introduced is negligible in character.

In the tables which follow, the symbols used have the following significance :

t_a = (corr.) temperature of the acid before mixing.

t_b = (corr.) temperature of the base before mixing.

W_1 = (corr.) water value of the acid.

W_2 = water value of the base + the solid parts in terms of water.

θ^4 = (corr.) mean temperature of the acid and base at time of mixing.

[1] Traité practique de Calorimétrie Chimique, p. 72 ff.

[2] *Loc. cit.*, 1, 52.

[3] *Loc. cit.*, p. 76.

[4] All temperatures are expressed in degress.

T = (corr.) maximum temperature of the mixture.

$\Delta\theta$ = rise in temperature.

Q = amount of heat given out, expressed in calories.

H = molecular heat of neutralization in calories.

For purposes of comparison with the numbers thus found, we have only the determinations made on pyridine by Colsen[1] and by Berthelot.[2] The former found for the heat of neutralization of pyridine (1 molecule in 2 liters) with hydrochloric acid (1 molecule in 1 liter), 5.2 Cal., while the latter obtained, using pyridine (1 molecule in 2 liters) and hydrochloric acid (1 molecule in 2 liters) at 22°, 5.1 Cal. The agreement between these investigators, using the same form of apparatus, is indeed very close, while the lower value obtained by us, 4.8 cal. seems not entirely comparable with that found by them. We are, nevertheless, inclined to insist upon the correctness of our number as expressing the true heat of neutralization of this substance. The fact that Colson and Berthelot, working at widely different temperatures, the latter at 22°, the former—who does not give the temperature of the surroundings—presumably, however (from the data given), about 13.°5–14°, obtained nearly the same value, leads to the conclusion that for pyridine hydrochloride the temperature influence is very small.[3] We may be allowed to surmise, therefore, that the discrepancy between their results and ours may be due to a difference in the character and purity of the bases used.[4]

From the results given in the table above it appears that both picolines have a higher heat of neutralization than pyridine, α-picoline giving a somewhat higher value than the β-compound. As will be shown below, the affinity-constants for the three substances follow the same order.

ELECTROCHEMISTRY OF THE PYRIDINE BASES.

The affinity constants for pyridine and α-picoline—also for *s*-collidine—have been determined by Goldschmidt and Salcher[5]

[1] Ann. chim. phys., [6], **19,** 411 (1890).

[2] *Ibid.,* **21,** 381.

[3] cf. Thomsen : *Loc. cit.,* p. 60.

[4] See, also, Kahlenberg, *Loc. cit.,* p. 287.

[5] Ztschr. phys. Chem., **29,** 89 (1899).

Table VIII.

No.	Substance.	t_a	t_b	W_1.	W_2.	θ.	T.	$\Delta\theta$.	Q.	H.	Mean.
1	Pyridine	17.767	17.358	298.50	307.1	17.558	18.735	1.177	713.42	4780.0	4776.2
2	"	17.868	17.606	298.92	"	17.735	18.914	1.180	715.09	4772.4	
3	α-Picoline	17.381	17.227	298.57	"	17.303	18.779	1.476	893.98	5988.5	5979.6
4	"	17.614	17.365	298.71	"	17.488	18.960	1.472	891.75	5970.7	
5	β- "	17.902	17.621	298.57	"	17.759	19.161	1.402	849.2	5688.4	5689.8
6	"	18.167	17.718	298.68	"	17.935	19.338	1.403	849.9	5691.1	

through a study of the aminolysis of these with aniline, using various acids; also, for pyridine, by measuring the hydrolytic dissociation of the nitrate.

Having at hand a supply of the very pure material used for the thermochemical investigations on these bases, and desiring to compare the three picolines as to their relative affinities, we have made measurements of the electrolytic conductivities of salts of these with this end in view.

Direct measurements of the conductivities of the bases themselves as a means of determining the affinities, did not promise to be successful, these being too small to give reliable values. Goldschmidt and Salcher attempted this with α-picoline, the most pronounced base of the series, without, however, obtaining very satisfactory results. It was, therefore, decided to make use of the hydrolytic method of Walker,[1] with application of the Arrhenius modification of the Guldberg-Waage law.[2]

For this purpose we sought to obtain a salt which could be prepared in a state of purity and which was sufficiently stable to allow the making up of solutions of definite concentration by weight. With the exception of pyridine—which forms a stable nitrate—none of these bases yield salts with the commoner acids ordinarily used in such measurements which are either sufficiently stable or sufficiently non-hygroscopic to be conveniently used for the above purpose. It is possible indeed to prepare, as Bredig has done in his measurements of the ionic conductivities of the bases, salts of these by neutralization in solution. It is very difficult, however, to do this in the case of those bases whose salts are hydrolytically dissociated, since these have an acid reaction towards indicators, even when equivalent amounts of acid and base are present. The preparation of neutral salts by weighing, when the substances are volatile, is likewise a difficult task.

The only one of the well-conducting acids which appears to form salts with these bases capable of being purified by recrystallization, and of being weighed out in exact quantities seems to be picric acid. This forms beautiful, well-crystal-

[1] Ztschr. phys. Chem., **4,** 319.
[2] *Ibid.*, **5,** 17.

lized compounds with pyridine and the picolines, and is itself almost completely dissociated at moderate dilutions.[1]

The picrates, therefore, seemed suited to the measurements of the hydrolytic and electrolytic dissociations of the salts of these bases; they possess, however, the very decided objection that they are all quite difficultly soluble, and it was, therefore, necessary to make use of solutions at such dilutions that the measurements become somewhat uncertain, owing to the influence of the water, etc. We found it impossible to prepare solutions stronger than 1 molecule in 128 liters, but as the measurements made with these agreed well and gave fairly satisfactory results in most cases up to 1 molecule in 1024 liters, we have used these for the calculation of the affinity-constants.

For the purpose of preparing the salts, the picric acid was first purified by recrystallization from water and finally by conversion into the sodium salt according to the method given by Lea.[2] The acid, as finally obtained, was tested as to its melting-point, $122°.5$, and its conductivity (see below). The salts were prepared in each case by making a concentrated solution of the acid, either in water or alcohol, and adding slightly more than the calculated amount of base, whereupon the picrates were immediately precipitated, the crystal mass filling the vessel. This was drained off by the aid of the pump, and the salt recrystallized, the pyridine and α-picoline picrates from water, the β- and γ-picoline picrates from alcohol. All yield difficultly soluble and well crystallized salts except the γ-compound, which crystallizes less well, and was more difficult to obtain pure, the best results being obtained by adding an excess of base and recrystallizing from strong alcohol. This behavior of the γ-salt is similar to that mentioned under the mercuric chloride salt (page 6), and the explanation there given can be applied to this as well. The melting-points obtained for the salts were: Pyridine picrate, $165°.5$; α-picoline picrate, $164°$; β-picoline picrate, $149°.5$; and γ-picoline picrate, $161°–162°$—the latter differing some-

[1] Ostwald: Ztschr. phys. Chem., **1**, 77 (1887); Bader: *Ibid.*, **6**, 289 (1890).

[2] Jsb., 1861, p. 635.

what from the melting-point given by Ladenburg, 167°.[1]

The water used in the measurements had a conductivity ranging between $0.9 \times 10.^{-6}$ and $1.5 \times 10.^{-6}$, and was obtained by a process of triple distillation through a battery of large retorts of Jena glass, so arranged that the neck of each served as a reflux condenser. The last retort was attached directly to a tin condenser; the entire apparatus was so connected that the distillate passed from one vessel into the other without coming in contact with the outer air. The distillation took place first from lime and permanganate, then from phosphoric acid, and finally from a nearly saturated solution of barium hydroxide. Before beginning the distillation, both ends of the apparatus were attached to a series of soda-lime tubes, and the air in the apparatus displaced by drawing through it a slow current of air freed from carbon dioxide. The supply water was introduced without opening the apparatus by means of a separatory funnel, the final distillate being siphoned off as needed. The supply water used had been previously distilled from a large tin still used only for such purposes. This water itself had a conductivity rarely exceeding $2 \times 10.^{-6}$. In all the conductivity measurements on the salts, the correction for water was brought into account as recommended by Ostwald.[2]

The conductivities were all determined at 25° C., the temperature being kept as exactly as possible at this point. The measurements are expressed in reciprocal Siemens units. An Arrhenius cell was used, the resistance capacity of which was determined after each series of measurements, using for this purpose a $N/50$ solution of potassium chloride.[3]

To test the method, measurements were first made upon the conductivities of pyridine and α-picoline picrates. Bredig, in his work upon the stoichiometry of the ions,[4] has determined the velocities of the pyridine and α-picoline ions, using the hydrochlorides for this purpose, while Goldschmidt and Salcher[5] have determined it for the pyridine ion, using the ni-

---

[1] Ann. Chem. (Liebig), **247**, 5.
[2] "Hand und Hilfsbuch", 2te Auf., p. 423.
[3] Ostwald : "Hand und Hilfsbuch", 1ste Auf., p. 273.
[4] Ztschr. phys. Chem., **13**, 191 ff. (1894).
[5] *Loc. cit.*

trate.   We, therefore, had in these determinations an oppor-
tunity of testing the suitability of picric acid for such pur-
poses, since, so far as known, it has not previously been so
made use of.

Ostwald[1] and Bader[2] have both measured the molecular con-
ductivity of picric acid, and the former that of sodium picrate.
The two determinations made on the acid do not agree and,
it furthermore appears probable that the velocity ascribed
by Ostwald to the picric ion, 31.5,[3] is too high by several
units.   We, therefore, decided to redetermine the velocity of
this ion, and used for this purpose the purified picric acid
mentioned above, as well as the sodium salt, which was sev-
eral times recrystallized from alcohol, its conductivity meas-
ured, and after a further recrystallization a second measure-
ment made ; the two agreed perfectly.   Each set of measure-
ments was made in duplicate.

Table IX.
Picric Acid, $C_6H_2(OH)(NO_2)_3 = 1 : 2 : 4 : 6.$
$$\mu_\infty = 356.$$

$v.$	$\mu_1.$	$\mu_2.$	Mean. $\mu.$
32	316.9	316.8	316.9
64	328.5	328.8	328.7
128	337.3	337.2	337.3
256	344.3	344.6	344.5
512	351.1	350.8	350.9
1024	357.7	357.5	357.6

Table X.
Sodium Picrate, $C_6H_2(NO_2)_3ONa.$
$$\mu_\infty{}^4 = 74.1.$$

$v.$	$\mu_1.$[5]	$\mu_2.$	$\mu_3.$	$\mu_4.$	Mean. $\mu_a.$	$\mu.$
32	62.1	62.2	62.3	62.2	62.2	62.1
64	64.2	64.0	64.2	64.2	64.2	64.1
128	65.7	65.7	66.0	66.0	65.9	65.7
256	67.2	67.4	67.8	67.6	67.5	67.2
512	69.0	69.8	69.4	69.5	69.4	68.8
1024	71.3	71.9	71.7	71.8	71.8	70.5

[1] *Loc. cit.*

[2] *Loc. cit.*

[3] Ostwald : Lehrbuch, **2**, 678.

[4] Calculated by use of Bredig's rule, Ztschr. phys. Chem., **13**, 198.

[5] μ_1 and μ_2 were obtained with the same solution ; μ_3 and μ_4 after further recrys-
tallization ; μ_a is the mean of all observations, and μ the corrected mean after deduct-
ing the conductivity of the water.

The values of μ_v for the acid are more nearly in accord with Bader's than with Ostwald's numbers, while for the salt, μ_v, for each concentration used, falls about 6 units below the value found at the corresponding dilution by Ostwald.

To calculate the velocity of the picric ion, we used the Kohlrausch law of the independent wandering of the ion,[1] expressed by the equation $\mu_\infty = a^\cdot + a'$, where $a^\cdot$ is the velocity of the cation and a' that of the anion at infinite dilution. To obtain from this the value of a' we have only to transform the equation to $a' = \mu_\infty - a^\cdot$; since both μ_∞ and $a^\cdot$ are known, the value of a' is also known.

The values of $a^\cdot_H$ and $a^\cdot_{Na}$ used were obtained from those given by Kohlrausch, expressed in reciprocal ohms and at 18°, *viz.*, $a^\cdot_H = 318$ and $a^\cdot_{Na} = 43.55$.[2] Our measurements having been made at 25° and in reciprocal Siemens units, the Kohlrausch values must be reduced to these conditions. For this purpose the temperature-coefficients α and β given by Kohlrausch were made use of and substituted in the temperature formula of Déguisne.[3]

$$K_t = K_{18}\left[1 + \alpha\,(t - 18) + \beta\,(t - 18)^2\right].$$

The value thus found, reduced to Siemens units by division by 1.066,[4] gives the desired number at 25°. The numbers thus found are $a^\cdot_H = 330$;[5] $a^\cdot_{Na} = 48.1$. Using the value $a^\cdot_{Na}$ thus found, we obtain as the value for $a'_{Pic.} = \mu_\infty - a^\cdot_{Na}$, the number 26.0.

In order to determine the conductivities, and also the hydrolysis, of the salts under consideration, three solutions of each were prepared by weighing off the calculated amount of the salt. One portion was dissolved in water, a second portion in a $N/32$ solution of the corresponding base, and the third portion in a $N/64$ solution of the same.[6] Duplicate measurements were made with each solution, the mean of

[1] Wied. Ann., **6**, 1 ; **26**, 213. Ostwald : Lehrbuch, **2**, 639. Bredig : Ztschr. phys. Chem., **13**, 194, 225.

[2] Sitzungsber : Kgl. preuss. Akad. Wiss., Berlin, 1901, p. 1031 ; 1902, p. 581.

[3] " Die Temperatur-coefficienten des Leitvermögens sehr verdünnter wässeriger. Lösungen." Dissertation, Strassburg, 1895.

[4] Kohlrausch, Holborn, aud Diesselhorst : Wied. Ann., **64**, 417 (1898).

[5] Compare Ostwald-Luther : "Hand und Hilfsbuch", p. 415.

[6] Bredig : Ztschr. phys. Chem., **13**, 214.

each series being here given under the respective headings μ_v (H_2O), $\overset{32}{\mu_v}$, and $\overset{64}{\mu_v}$ (for the solutions in N/32 and N/64 solution of base). In series μ_v pure water was used in making the dilutions. In the series $\overset{32}{\mu_v}$ and $\overset{64}{\mu_v}$ the dilutions were made with N/32 and N/64 solutions of the base respectively.

By this method—the conductivity of the base itself being so small as to be negligible, as compared with that of the salt—the hydrolysis was practically annulled and the necessary conditions to the equation $M_v = \mu_v{}^1$ fulfilled. As may be seen from the tables, the values of $\overset{32}{\mu_v}$ and $\overset{64}{\mu_v}$ are nearly identical, and we can therefore assume the mean of the two, μ_v, as the true electrolytic conductivity.

In order to save space, the values $100x$ and $\dfrac{K_3}{K_4}$, which are to be considered later, are inserted in the same tables.

<div align="center">

Table XI.

Pyridine Picrate, $C_6H_2(NO_2)_3O.HNC_5H_5$.

$\mu_\infty = 72.4$.

</div>

$v.^2$	$M_v.$	$\overset{32}{\mu_v.}$	$\overset{64}{\mu_v.}$	Mean. $\mu_v.$	$100x.$	$\dfrac{K_3}{K_4}.$
128	70.58	64.51	63.66	64.09	2.38	221×10^3
256	74.95	66.29	66.35	66.32	3.10	258×10^3
512	80.01	68.48	67.94	68.21	4.17	282×10^3

<div align="right">

Mean, 253×10^3

</div>

<div align="center">

Affinity-constant, $253 \times 10^3 \times 1.2 \times 10^{-14} = 3.0 \times 10^{-9}$

Table XII.

α-Picoline Picrate, $C_6H_2(NO_2)_3O.HNC_6H_7$.

$\mu_\infty = 66.8$.

</div>

$v.$	$M_v.$	$\overset{32}{\mu_v.}$	$\overset{64}{\mu_v.}$	Mean. $\mu_v.$	$100x.$	$\dfrac{K_3}{K_4}.$
128	60.71	58.34	58.41	58.38	0.84	1819×10^3
256	63.64	60.68	60.64	60.66	1.05	2297×10^3
512	66.61	63.51	63.15	63.33	1.14	3892×10^3

<div align="right">

Mean, 2669×10^3

</div>

<div align="center">

Affinity-constant, $2669 \times 10^3 \times 1.2 \times 10^{-14} = 3.2 \times 10^{-8}$

</div>

[1] See Bredig : *Loc. cit.*

[2] The values at v 1024 are omitted, as the agreement at this dilution was not very satisfactory.

Table XIII.

β-Picoline Picrate.

$$\mu_\infty = 68.4.$$

v.	M_v.	$^{32}\mu_v$.	$^{64}\mu_v$.	Mean. μ_v.	$100x$.	$\dfrac{K_3}{K_4}$.
128	63.64	59.83	59.93	59.88	1.35	687×10^3
255	67.20	62.29	62.16	62.23	1.76	811×10^3
512	70.97	65.24	64.61	64.93	2.10	1131×10^3

Mean, 876×10^3

Affinity-constant, $876 \times 10^3 \times 1.2 \times 10^{-14} = 1.1 \times 10^{-8}$

Table XIV.

γ-Picoline Picrate.

$$\mu_\infty = 66.3.$$

v.	M_v.	$^{32^1}\mu_v$.	μ_v.	$100x$.	$\dfrac{K_3}{K_4}$.
128	62.43	57.99	57.99	1.59	498×10^3
256	65.29	60.22	60.22	1.78	791×10^3
512	68.30	62.75	62.73	1.87	1440×10^3

Mean, 909×10^3

Affinity-constant, $909 \times 10^3 \times 1.2 \times 10^{-14} = 1.1 \times 10^{-8}$

Using the value for the picric ion given above, and substituting this in the equation $\mu_\infty = a\cdot + a'$, we obtain the following numbers expressing the velocities of the respective cations:

			Bredig.[2]	Goldschmidt and Salcher.[3]
Pyridine	$a\cdot$	46.4	44.1	44.4
α-Picoline	$a\cdot$	40.8	39.1	
β- "	$a\cdot$	42.8		
γ- "	$a\cdot$	40.3		

Although our numbers fall somewhat higher than those obtained by Bredig and by Goldschmidt and Salcher, considering the fact that we have used in our calculations Kohlrausch's most recent values expressing the velocities of the ions at in-

---

[1] The amount of material at our disposal was not sufficient to make the measurements in the N/64 solution of the base.

[2] *Loc. cit.* p. 231.

[3] Calculated from the data given by Goldschmidt and Salcher: *Loc. cit.*

finite dilution—those values differing somewhat from the ones used by the authors mentioned—the agreement must be regarded as of a satisfactory nature.

If we add to the numbers given above the value for the OH ion at infinite dilution, we obtain the values expressing the conductivities of the respective bases. Using Kohlrausch's value for $a'_{OH} = 174$, and calculating this to 25° and in Siemens units according to the method already described, we obtain 183.7. The bases, therefore, have the conductivities at infinite dilution expressed by the following numbers :

Pyridine hydrate,	C_5H_5NHOH	230.1
α-Picoline hydrate,	C_6H_7NHOH	224.5
β-Picoline hydrate,	C_6H_7NHOH	226.5
γ-Picoline hydrate,	C_6H_7NHOH	224.0

On comparing the velocities of the cations as given above, it will be evident that also for the cations of the pyridine series, the general rule suggested by Ostwald, and further developed by Bredig,[1] *viz.*, that " isomeric ions have the same velocities of transport," holds good, for the three picolines have approximately the same values. Attention may be called to the fact that the β-compound has a value differing slightly from the others, a condition which is also exhibited by the ion of meta compounds in general (see Bredig's table). This is in accord with the variation in the heats of combustion to which attention has previously been called. Bredig has also shown that the law of like velocities of transport does not hold good for the metamers (Cf. aniline, $a' = 38^2$).

For a determination of the relative affinities of the bases, the velocity method, which depends upon the rate at which saponification of an ester such as methyl acetate takes place, seemed excluded because the bases in question were not weak enough to admit of the application of the law of mass action, being considerably stronger than aniline.[3]

The measurement of the extent of hydrolysis of the salts, as determined electrolytically, promised to give somewhat

[1] *Loc. cit.*, 247 ff.

[2] To make the values comparable, the speed of aniline, 35.9, given by Bredig has been raised about 2 units.

[3] Walker : Ztschr. phys. Chem., **4**, 327 (1889).

more satisfactory results, although even here it was not to be expected that the constants expressing the ratios between the dissociation of the base and that of water would be found of a completely satisfactory character, since the hydrolysis is too slight to give a sufficient difference between the conductivities of the non-hydrolyzed salt and that in which hydrolysis had taken place. Slight errors of observation under these conditions affect enormously the end result.[1] By working at higher temperatures, thus increasing the extent of the hydrolysis, this might have been obviated in part. Unfortunately, the time at our disposal did not permit of this being done.

Under these conditions the results as given cannot be considered as sufficiently accurate to indicate the absolute affinities, but suffice to give a qualitative measure of these, and to furnish a comparison between the affinities of these bases themselves.

The method used was that given by Walker[2] and containing the Arrhenius modification of the Guldberg-Waage law,[3] as expressed by the equation :

$$\frac{K_3}{K_4} = \frac{v(1-x)}{x^2},$$

where

$v =$ the volume in liters containing 1 gram-molecule of the salt.

$x =$ the degree of dissociation of the salt, assuming the amount originally present as 1.

$K_3 =$ the dissociation or affinity-constant of the base.

$K_4 =$ the dissociation-constant of water.

The value of x can be determined by means of the conductivity of the hydrolytically dissociated salt, using the method suggested by Bredig,[4] in which, in order to obtain the true electrolytic conductivity (that in which no hydrolysis is present), a solution of the weak base is used as solvent and for dilution purposes. Expressing the conductivity of the

[1] Bredig: *Loc. cit.*, 324, 325.
[2] *Loc. cit.*, p. 333.
[3] Ztschr. phys. Chem., **5**, 17 ; see also Bredig : *Ibid.*, **13**, 321.
[4] *Loc. cit.*, p. 213.

hydrolytically dissociated salt by M_v, that of the electrolytically dissociated salt by μ_v, and that of the acid by μ_A, the value of x can be determined from the formula

$$M_v = (1-x)\mu_v + x\mu_A,$$

or

$$x = \frac{M_v - \mu_v}{\mu_A - \mu_v}.$$

Substituting, in this expression, the values found for the picrates as given in the table under M_v and μv, and the value μ_A of picric acid for the corresponding dilution, we obtain the values of x for each dilution and from these that of $\frac{K_3}{K_4} =$ constant.

As has been remarked, the values of $\frac{K_3}{K_4}$ found are not exactly constant, and for the reasons already stated. They serve, however, to give an approximate value from which that of K_3, the affinity-constant can be obtained by multiplication by 1.2×10^{-14} expressing the dissociation-constant K_4 of water.[1] The affinity-constants thus obtained, *viz.*,

Pyridine	$3.0.10^{-9}$
α-Picoline	$3.2.10^{-8}$
β-Picoline	$1.1.10^{-8}$
γ-Picoline	$1.1.10^{-8}$

are, in all probability, somewhat too high. That of γ-picoline undoubtedly is, for other considerations—notably, the behavior of salts of the two bases—indicate that it is somewhat weaker than the β-compound.[2] For the others, the affinities follow in the same order as the heats of neutralization already given.

The values found for pyridine and α-picoline agree fairly well with those obtained by Goldschmidt and Salcher, pyridine, $2.4.10^{-9}$; α-picoline, $4.5.10^{-8}$.

[1] van't Hoff: Vorlesuugen, I, 127.
[2] This is, perhaps, to be accounted for in part by the difficulty of preparing a pure γ-salt, that obtained apparently still containing traces of the base, from which it was not possible to rid it by washing with alcohol.
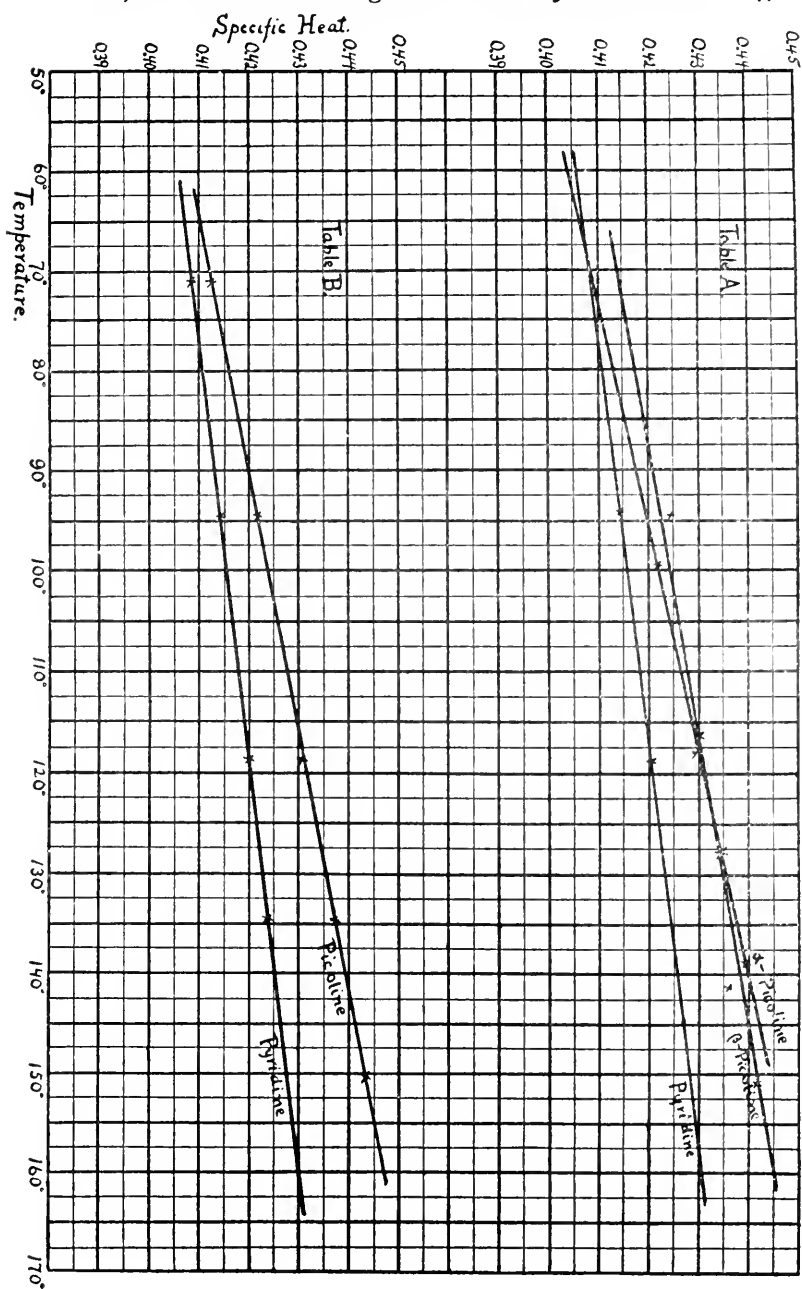
Table XV.

n_{Na} = specific refraction.

Substance.	Density.		Brühl.		C. and W.		$\left(\dfrac{n^2-1}{n^2+2}\right)\dfrac{M}{d\frac{t}{4°}} = m$ = mol. refraction.	
	Brühl. $\frac{20°}{4°}$	C. and W. $\frac{15°}{4°}$	$t.$	$n.$	$t.$	$n.$	Brühl.	C. and W.
Pyridine	0.9800	0.9893	18°.6	1.51026	17°.3	1.51068	24.09	23.94
α-Picoline	0.9451	0.9497	16°.7	1.50293	17°.1	1.50237	28.98	28.95
"	....	....	....	....	18°.0	1.50225	....	28.95
β- " "	0.9579	0.9613	24°.0	1.50432	18°.1	1.50720	28.83	28.83
γ- " "	....	0.9571	....	....	17°.0	1.50640	....	28.92

MOLECULAR REFRACTION OF THE PYRIDINE BASES.

In order to further test the condition of purity of our substances, we made use of the simple and accurate method of Pulfrich, whereby the refractive index of the substance under consideration is obtained, from which, in turn, the molecular refraction can be calculated. Brühl, in his classical researches in this direction, had already measured the refractive indices of pyridine, α- and β-picoline.[1] It pleases us to be able to confirm his results in every particular, as a glance at the comparative table shows :

Summing up the results of the above investigation, we arrive at the following conclusions :

(1) That the regularity in the increase of the heats of combustion between homologues, observed in the aliphatic and aromatic series extends also to the pyridine compounds, being found equal to 156 cal. for each CH_2.

(2) That the heat of formation of pyridine and its homologues can be approximately calculated from the formula,

$$C_nH_{2n-5}N = -51.7 \text{ cal.} + n7 \text{ cal.}$$

(3) That Trouton-Schiff's rule $\dfrac{MH}{T} =$ constant, holds good

for the pyridine series also.

(4) That the affinities of pyridine and the picolines are of approximately the same order as that of p-toluidine.

LABORATORY OF PHYSICAL CHEMISTRY,
  FEDERAL POLYTECHNICUM, ZURICH,
    SWITZERLAND,
      July, 1902.

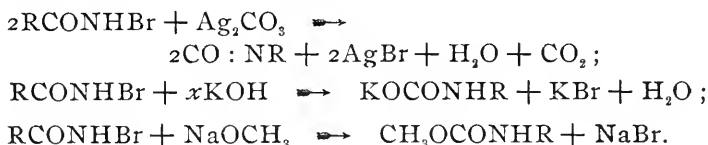## ON THE "BECKMANN REARRANGEMENT."[2] II.

BY JULIUS STIEGLITZ.

The molecular rearrangement which has come to be known as the "Beckmann rearrangement" has been produced in three classes of nitrogen derivatives: The acid halogen amides, $RCON^*H(Hal)$, the oximes of ketones, aldehydes,

[1] Ztschr. phys. Chem., **16**, 214.
[2] The first paper was published in this JOURNAL, **18**, 751 (1896).

acid salts, amides, and esters, $RR'C : N^*OH$),[1] and the acid azides,[2] $RCON^*(N_3)$. In every case the essential point of the rearrangement is that the alkyl (alphyl) group, R, is made to leave the carbon atom which holds it in the original substance and is then found joined to the nitrogen atom, N^*, derivatives of an alkyl (alphyl) amine being formed. The following instances may be used in illustration : Acid bromamides on treatment with silver carbonate,[3] alkalies,[4] or sodium methylate[5] produce cyanates, carbamates, and urethanes, respectively :

$$2RCONHBr + Ag_2CO_3 \longrightarrow$$
$$2CO : NR + 2AgBr + H_2O + CO_2 ;$$
$$RCONHBr + xKOH \longrightarrow KOCONHR + KBr + H_2O ;$$
$$RCONHBr + NaOCH_3 \longrightarrow CH_3OCONHR + NaBr.$$

Acid azides, on warming with alcohols, give urethanes :[6]

$$RCON(N_2) + HOCH_3 \longrightarrow CH_3OCONHR + N_2.$$

The dry alkali salt of an acylhydroxamic acid breaks down spontaneously, yielding an isocyanate :[7]

$$RC(OK) : N(OCOR') \longrightarrow CO : NR + KOCOR'.$$

Ketoximes, on treatment with certain dehydrating reagents, give acid amides :

$$RR'C : NOH \longrightarrow R'CONHR.$$

The determination of the essential cause and mechanism of these rearrangements is a problem of deepest interest which still awaits its final solution, although it has already been the subject of some investigation and speculation. In a paper published in this JOURNAL six years ago the author developed a theory as to the nature and cause of the rearrangement, and

---

[1] R' may be hydrogen, an alkyl, an alphyl, an alkoxyl group, a metaloxyl group, OMe', or an amide group.

[2] An alkyl azide, benzylazide, also has been found to react in the same fashion. Curtius : J. prakt. Chem., **63**, 429 (1901).

[3] Hofmann : Ber. d. chem. Ges., **15**, 412 (1882).

[4] Hoogewerff and van Dorp : Rec. trav. chim. Pays-Bas, 8, 200 (1887).

[5] Lengfeld and Stieglitz : This JOURNAL, **15**, 214, 504 (1893).

[6] Curtius : Ber. d. chem. Ges., **27**, 778 (1894) ; J. prakt. Chem., **50**, 289 (1894).

[7] Unpublished results of Dr. L. W. Jones, of this university. See also Hantzsch : Ber. d. chem. Ges., **27**, 1256 (1894) ; Thiele : Ann. Chem. (Liebig), **309**, 189 (1899).

outlined certain points of attack which promised to lend themselves to the experimental investigation of the correctness of the theory. The work has progressed very slowly, largely because an important part was undertaken in collaboration with Mr. E. E. Slosson, of the University of Wyoming, and the latter was able to devote only his summer vacations to the prosecution of the investigation. The work with Mr. Slosson having now reached a certain stage of completeness, it is proposed in this paper to consider the present aspect of our knowledge of the " Beckmann rearrangement" on the basis of all the general facts known in connection with it, and particularly on the basis of the results obtained with Mr. Slosson, as well as in shorter investigations carried out with Drs. O. Folin, H. H. Higbee, H. N. McCoy, J. H. Ransom, and Elizabeth Jeffreys.[1]

It may be said that any interpretation of the "Beckmann rearrangement" must take cognizance of these fundamental points :

(1) The nature of the rearrangement of the three classes of nitrogen derivatives described above seems to be substantially the same. This follows from the strictly analogous character of the initial substances, from the adaptation of the reagents used in effecting the rearrangement to the variation in the elements combined with the nitrogen in the compounds used, and from the frequent identity and otherwise close relationship of the products obtained from all three classes of compounds.
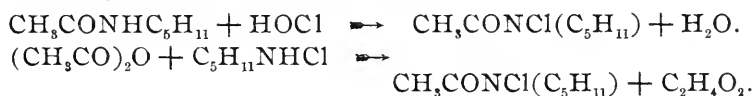
(2) The rearrangement is produced by reagents which stand in the most intimate relation to the elements combined with the nitrogen in each of the classes of nitrogen compounds under investigation. In the case of the acid halogen amides, $RCONH(Hal)$, the effect is produced by substances which have the greatest affinity for the halogen acids—for instance the alkalies and silver carbonate—and salts of these acids are always obtained in the reaction. The halogen atoms go from the condition of "hypo-acid" radicals[2] into simple negative

---

[1] Beckmann : Ber. d. chem. Ges., **19**, 988, etc. (1886).

[2] Seliwanow: *Ibid.*, **25**, 3620 (1892).

ions and their salts. Van Dam[1] has shown, in fact, that the velocity of the rearrangement is proportional to the concentration of hydroxyl ions in the solution. The rearrangement of the oximes of ketones, aldehydes, and acid esters is effected by dehydrating reagents, water or derivatives of water resulting.[2] The rearrangement of the acylhydroxamic acids, $RCONH(OCOR')$, on the other hand, is again caused by alkalies, salts of the organic acids, $HOCOR'$, being formed. Finally, the rearrangement of the acid azides, $RCON(N_2)$, requires no such reagent; it is produced essentially by the action of heat, nitrogen being evolved in all such cases.

(3) When in the case of the acid bromamides, $RCONH^*Br^*$, the possibility of the loss of hydrobromic acid by the union of the atoms marked * in the formula is cut off by replacing the hydrogen atom by an alkyl or an alphyl group, the tendency to undergo the "Beckmann rearrangement" has been found also to be entirely suppressed. Mr. Slosson and I have shown this to be the case for the acylalkylhalogenamines[3] whose constitution we determined by the preparation of identical substances by the action of hypochlorous acid on acetylamyl-amine, on the one hand, and of acetic acid anhydride on chloramylamine, on the other hand:

$$CH_3CONHC_5H_{11} + HOCl \longrightarrow CH_3CONCl(C_5H_{11}) + H_2O.$$
$$(CH_3CO)_2O + C_5H_{11}NHCl \longrightarrow$$
$$CH_3CONCl(C_5H_{11}) + C_2H_4O_2.$$

Chlorimidoesters, $RC(:NCl)OR'$, also have lost the tendency[4] to suffer the molecular rearrangement so characteristic of the parent substances, the acid halogenamides. In like fashion, according to an investigation carried out by Dr. Higbee, at my suggestion, derivatives of the oximes, in which the possibility of the breaking off of water from a trivalent nitrogen atom is excluded, refuse to undergo the rearrangement when treated with the same dehydrating reagents which

---

[1] Rec. trav. chim. d. Pays-Bas., **18**, 408 (1899); **19**, 318 (1900). In the same investigation Van Dam proved that the reaction is a monomolecular one, the rearrangement, therefore, intramolecular.

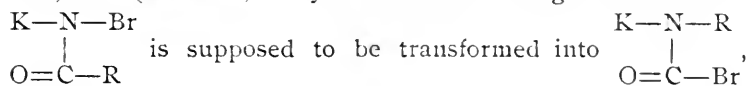[2] See this JOURNAL, **18**, 754 (1896). Foot-note.

[3] See the article in a later number of this JOURNAL, and preliminary reports: Ber. d. chem. Ges., **28**, 3266 (1895); **34**, 1613 (1901).

[4] *Loc. cit.*, and Stieglitz, This JOURNAL, **18**, 751 (1896).

are so effective in the case of the ketoximes. β-Benzoyl-β-phenylhydroxylamine, $C_6H_5CON(C_6H_5)OH$, under such treatment does not give the least discernible trace of diphenylamine, and yet the color test for this substance belongs to the most sensitive known in organic chemistry.

On the basis of these general facts and with the aid of a number of other experimental facts which will be referred to in the course of the discussion, the most important of the theories advanced in explanation of the "Beckmann rearrangement" may be critically considered.

A. W. Hofmann, whose work on the acid bromamides gave us the first instances of this molecular rearrangement, never suggested any explanation of the important reaction he discovered. Hoogewerff and van Dorp,[1] who continued Hofmann's work with great skill, advanced the first hypothesis as to the nature and cause of the rearrangement of the acid bromamides, to whose alkali salts they assigned the constitution, $RCO(NMe'Br)$. By intramolecular migration the salt

$$\begin{matrix} K-N-Br \\ | \\ O=C-R \end{matrix} \quad \text{is supposed to be transformed into} \quad \begin{matrix} K-N-R \\ | \\ O=C-Br \end{matrix},$$

which in turn is decomposed into potassium bromide and an isocyanate. The transposition is said to be caused, in particular, by the tendency of nitrogen to combine with radicals more positive than the halogens. In support of their view these chemists point out that the intramolecular migration must depend largely on the nature of the group R. When this group becomes more negative the transposition must become more difficult. Observations made at the time the theory was advanced confirmed this conclusion ; the salts of the nitrobenzbromamides were found to be more stable than those of benzbromamide. It was found later, however, by McCoy and myself,[2] that dibromsalicylicbromamide, in which R is the exceedingly negative radical $C_6H_2Br_2(OH)'$, suffers the rearrangement even below $5°$, in the course of a few sec-

---

[1] Rec. trav. chim. Pays-Bas., **6**, 373 (1887) ; **8**, 173, etc. (1889) They were the first to call attention to the similarity of Hofmann's reaction and the "Beckmann rearrangement" of the oximes. See also : Graebe and Rostovzeff : Ber. d. chem. Ges., **35**, 2747 (1902) ; Hantzsch : *Ibid.*, **35**, 3579 (1902).
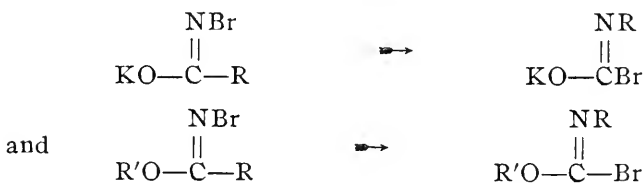
[2] This JOURNAL, **21**, 116(1899).

onds, so rapidly that the bromamide could not be isolated. Van Dam,[1] in Hoogewerff and van Dorp's laboratory, obtained exactly the same results working at $-12°$, independently of, and almost simultaneously with, the work done in this laboratory. As to the main point in Hoogewerff and van Dorp's hypothesis, the theory fails to adapt itself to the entirely analogous behavior of the acid azides and acid bromamides, and to explain the fact that acylalkylhalogenamines do not rearrange.[2] One would expect the intramolecular transposition of the bromine and the alkyl R, as in

$$CH_3-N-Br \qquad\qquad CH_3-N-R$$
$$\qquad| \qquad\qquad\longrightarrow \qquad\qquad | \qquad,$$
$$O=C-R \qquad\qquad\qquad O=C-Br$$

to occur quite as easily as in the case of the alkali salts (see the equation above), if it is merely a matter of the relative affinity of nitrogen for alkyls and halogens, respectively.

The alkali salts of the acid bromamides are now recognized as having a different constitution from that assigned originally to them by Hoogewerff and van Dorp. The constitution[3] is now known to be $RC(OMe) : NBr$. But even the esters corresponding to such salts, the chlor- and bromimido esters, do not undergo the "Beckmann rearrangement." The reactions

$$\overset{NBr}{\underset{KO-C-R}{\|}} \qquad\longrightarrow\qquad \overset{NR}{\underset{KO-CBr}{\|}}$$

and

$$\overset{NBr}{\underset{R'O-C-R}{\|}} \qquad\longrightarrow\qquad \overset{NR}{\underset{R'O-C-Br}{\|}}$$

would be strictly analogous, according to the Dutch chemists' interpretation, but the second reaction does not take place. In conclusion, the important function of the reagents which produce the rearrangement of the acid bromamides (see page 51), seems to find no place in this theory.[4]

[1] *Loc. cit.*

[2] Stieglitz and Slosson : *Loc. cit.*

[3] See below, page 64.

[4] NOTE : In a short article (Ber. d. chem. Ges., **35**, 3579 (1902)) published after this paper was written, Hantzsch, while accepting Hoogewerff and van Dorp's in-
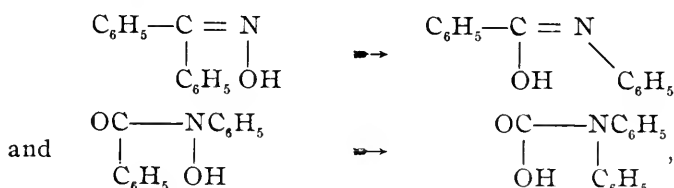
Beckmann, the discoverer of the molecular rearrangement of the oximes of ketones and aldehydes, whose name is now used to designate this typical transformation, advanced an explanation[1] of the reaction in 1894, which is very much like the one just discussed. He suggested, rather vaguely, that the rearrangement might consist simply in the transposition of electrically charged radicals or ions, and that the dehydrating reagents employed act chiefly, although not wholly, as catalytic agents giving the necessary impetus for a change from a labile to a stable condition. In the reaction

$$(C_6H_5)_2C : NOH \quad \longrightarrow \quad C_6H_5C(OH) : NC_6H_5$$
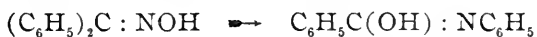
a direct exchange of the phenyl and hydroxyl groups is assumed. The theory is essentially a restatement of obvious results obtained with only one class of compounds, the oximes. Like the previous theory, it fails to explain, on the one hand,

terpretation of the rearrangement, suggests that the rearrangement of the acid bromamides is caused by an alkali essentially because the latter is necessary to produce a double bond between the acyl carbon and the nitrogen. Whereas the acid bromamides have the constitution, $RCO.NHBr$, the salts have the constitution $RC(ONa) : NBr$, (see page 64), which is said to bring them into much closer analogy with the oximes. The rearrangement is supposed to proceed then by an exchange in position of the alkyl R, and the bromine atom. This possibility that a double bond might be an essential condition for the rearrangement, and might explain best the rearrangement of the stereoisomeric oximes was the chief reason for the study of the chloro- and bromimido esters, $RC(OR) : NHal$, by the author (see the first paper, this JOURNAL, 18, 751 (1896), and the article by Mr. Slosson in a later number of this JOURNAL). They were found to be remarkably stable nitrogen halides which not only do not suffer a "Beckmann rearrangement" spontaneously at ordinary temperatures (as do the salts of the acid bromamides), but they do not even rearrange on warming to 100° to 140°. In fact, they have never, as yet, been observed to rearrange under any condition whatsoever. Stereoisomers do not seem to exist, and preliminary experiments, which will be continued by Mr. Test, indicate that the acid chloramides produce, on the one hand, with diazomethane the stable chlorimido esters, and, on the other hand, with alkalies the easily rearranged salts. These facts show that the double bond is, after all, not the vital factor that Hantzsch assumes, and that the effect of the alkali must be something essentially more than to produce a double bond. The ready and sometimes spontaneous rearrangement of acylhydroximic acid salts, $RC(ONa) : NOAcyl$, and the marked stability of the corresponding esters, $RC(OR') : NOAcyl$, (the acetyl ester of ethylsynbenzhydroximic acid can be heated to 140° without change, according to Werner: Ber. d. chem. Ges., 25, 41 (1892)), emphasize the same point. Hantzsch's assumption of the intermediate formation of a chlorimide, $R_2C : NCl$, in the rearrangement of the ketoximes under the influence of phosphorus pentachloride also appears unwarranted in view of the above facts, and in view of the further fact that other acid dehydrating reagents have the same effect. Finally, the acyl azides have no double bond between carbon and nitrogen and yet they are rearranged with remarkable smoothness.

[1] Ber. d. chem. Ges., 27, 300 (1894).

the analogous behavior of the oximes and acid azides, and, on the other hand, the complete difference in behavior of compounds most closely allied to the oximes, such as β-benzoyl-β-phenylhydroxylamine. There is no evident reason, according to Beckmann's view, why both the following reactions should not occur with equal ease :

$$C_6H_5-C = N \atop \overset{|}{C_6H_5}\ \overset{|}{OH} \quad \longrightarrow \quad C_6H_5-C = N \atop \overset{|}{OH}\ \diagdown_{C_6H_5}$$

and
$$OC\!\!-\!\!-\!\!NC_6H_5 \atop \overset{|}{C_6H_5}\ \overset{|}{OH} \quad \longrightarrow \quad OC\!\!-\!\!-\!\!NC_6H_5 \atop \overset{|}{OH}\ \overset{|}{C_6H_5} ,$$

and yet the second reaction does not take place even to a slight extent. Finally, the characteristic adaptation of the reagent effecting the rearrangement to the class of nitrogen compounds used (see page 51), is also left practically out of consideration in this interpretation.

In an unpublished investigation carried out at this university in 1896, Dr. Bernhard C. Hesse examined experimentally the reliability of an entirely new explanation of the "Beckmann rearrangement," based on the following views : It was thought possible that the transformation of acetbromamide, for instance, was accomplished through the following stages :

$$CH_3CONHBr + 2KOH \longrightarrow$$
$$\underline{CH_2-CO-NH} + KBr + KOH \longrightarrow$$

$$KOCONHCH_3 + KBr.$$
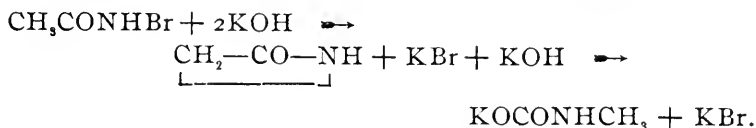
The intermediate formation of a triatomic ring was the basis of the explanation, in analogy to similar known changes of position of alkyls through the intermediate formation of trimethylene rings. Dr. Hesse has kindly consented to let me publish the results of this investigation.

The reliability of the theory was tested by studying the rearrangement-product of trimethylacetbromamide, $(CH_3)_3C.$ CONHBr. An intermediate triatomic ring formation being impossible in this case, at best a tetratomic ring could result. In the latter event isobutylamine, $(CH_3)_2CHCH_2.NH_2$, would

be the final product, while if no ring formation at all occurred, tertiary butylamine, $(CH_3)_3C.NH_2$, would be formed. Dr. Hesse identified the salts obtained as those of tertiary butylamine, thus disposing of the possibility that intermediate unstable ring formations of the nature indicated are the cause of the rearrangement.

It may be added that a triatomic ring, as used in the above equation would, doubtless, open between the carbonyl and the imide groups, as all acid amides are saponified in this way.

Only a very brief reference need be made to the views of Freundler.[1] He suggests that the rearrangement of the acid bromamides could be due to a series of reactions, the essential feature of which is the intermediate formation of carbylamine and hypobromite. These views were suggested by the erroneous idea that an isocyanate had never been isolated as an intermediate product in Hofmann's reaction. It is hardly necessary to add that none of Freundler's supposed intermediate products have ever been isolated in the reaction under discussion, and that it would be impossible to bring his views into accord with the behavior of the acid azides and the acylhydroxamic acid salts.

The most recent suggestion as to the nature of the "Beckmann rearrangement" has been made, incidentally, by Nef[2] in connection with an exhaustive study of dissociation phenomena of alcohols, ethers, and organic acid salts. Having shown that an alkylidene residue, $RCH=$, or a phenylene group, $C_6H_4=$, is often broken off from one of the above compounds, and sometimes absorbed again in a different position from that occupied in the original molecule, Nef suggests that the rearrangement of the acid bromamides and of the oximes is due to similar changes. For instance, acetbromamide is supposed to undergo the following series of changes :

$$CH_3CONHBr \ \rightarrowtail \ CH_2: + HCONHBr \ \rightarrowtail$$
$$HCO(NCH_3Br) \ \rightarrowtail \ OC:NCH_3 + HBr.$$
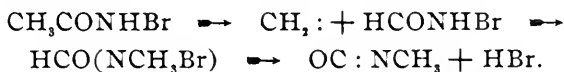
Further close investigation may, possibly, be needed abso-

[1] Bull. Soc. Chim., **17**, 421 (1897).

[2] Ann. Chem. (Liebig), **298**, 308 (1897) ; **318**, 39, 227 (1901).

lutely to prove or disprove the correctness of this interesting view and, with the consent of Dr. Nef, experiments lending themselves to a further test of the theory will be carried out. At present, however, it may be said that it cannot be applied directly to the acid azides, and that it leaves quite out of consideration the fact that the nature of the reagents, used to effect the molecular rearrangement in each of the three classes of compounds under discussion, stands obviously in closest relation to the elements or groups combined with the nitrogen, and not to the alkyl or alphyl group attached to the acyl carbon atoms (see page 51). The most important difficulty, however, in the way of Nef's view is that in every product of the " Beckmann rearrangement" known to the author, the nitrogen atom is found to occupy exactly the same position in the alkyl chain or alphyl nucleus which was held originally by the carbon atom that separated the migrating alkyl or alphyl group from the nitrogen atom. Thus, trimethylacetbromamide, $(CH_3)_3C.CONHBr$, according to the work of Dr. Hesse reported above, gives tertiary butylamine, $(CH_3)_3C.NH_2$, and not isobutylamine, $(CH_3)_2CHCH_2NH_2$, and the three nitrobenzbromamides, para, meta, and ortho, give the corresponding para-, meta-, and orthonitranilines or their derivatives.[1] This is not necessary and hardly possible always, according to Nef's view, for derivatives of tertiary and aromatic acids, ketones and aldehydes are supposed by him to dissociate into olefines or phenylenes,[2] as the methylene dissociation is excluded, and these residues are said to act as the methylene does in the above reaction. Under such circumstances one would have to expect that metanitrobenzbromamide would give, to a considerable extent, the same aniline derivatives as either ortho- or paranitrobenzbromamide, from the reactions :

[1] Hoogewerff and van Dorp : Rec. trav. chim., Pays-Bas, 8, 193, 196, 199 (1889) ; Lengfeld and Stieglitz : This JOURNAL, 16, 371 (1894) ; Folin : *Ibid.*, 19, 325, etc., (1897); Swartz ; *Ibid.*, 19, 303 (1897) ; Jeffreys : *Ibid.*, 22, 41 (1899) : Struve and Radhausen : J. prakt. Chem., 52, 230 (1895).
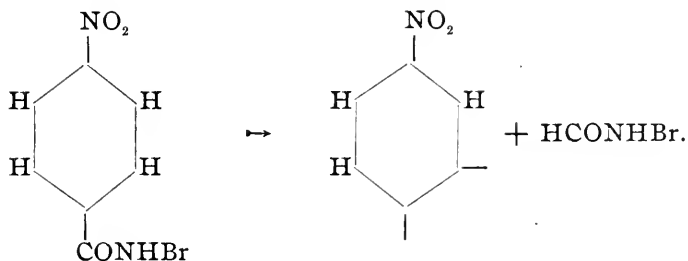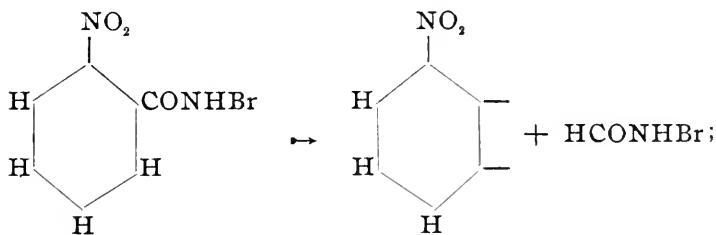[2] Nef : *Loc. cit.*
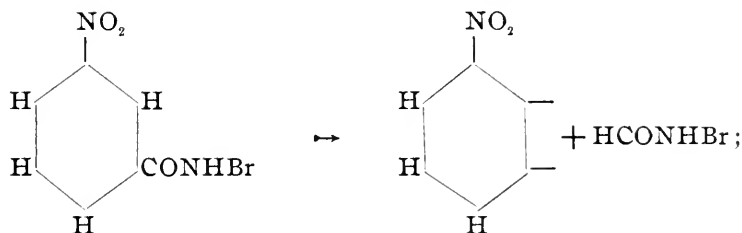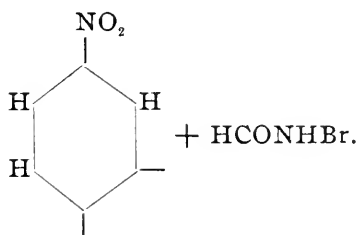
The same intermediate nitrophenylene must result as from either one or the other of the following dissociation reactions:

But, as a matter of fact, each nitrobenzbromamide gives exclusively an excellent yield of the corresponding nitraniline

or its derivatives.[1] Whether traces or very small quantities of the isomers are also formed remains a question for further investigation. One would expect, however, not traces but considerable quantities of identical substances in view of the above discussion.

The actual dissociation tendency of compounds of the general type, $RR'NX$, in which X is a halogen, a hydroxyl or an acid group, RCO, as will be shown below, has been observed in a number of instances to be rather toward the breaking off of $R'X$ from the molecule, leaving most likely an unsaturated imide group with univalent nitrogen, $RN=$, as a primary but unisolated product of dissociation. Such a result would be analogous to the alkylidene formations exhaustively studied by Nef. It seems at present, therefore, that the conceptions of " methylene and phenylene dissociations" will aid in clearing up the problem of the " Beckmann rearrangement" rather by analogy than by direct application.[2]

The last interpretation of this molecular rearrangement to be discussed is that proposed by the writer in 1896, the experimental study of which forms the basis of this paper. It may be briefly stated as follows: Starting out from the pronounced similarity in the behavior of the parallel classes of derivatives, $RCONHBr$, (I.), $RCONH(OCOR)$ (II.), or $R_2C(NOH)$, (II'.), and $RCON(N_2)$, (III.), an initial change which could be common to all three classes of compounds was sought and found in the possibility of all three series of compounds easily yielding an identical intermediate derivative (for instance, $(RCO)N=$), with univalent nitrogen. The first class would do so by the initial loss of hydrobromic acid; the second, (II.), by the loss of an organic acid, $HOCOR$, or (II'.), by the loss of water from salts[3] such as the hydrochlorides, $R_2CCl.NHOH$, the result being $R_2CCl.N=$; the third, simply by that loss of nitrogen which is so common with diazo derivatives.

The nature of the reagents used to effect the rearrangement is in complete agreement with this conception, alkalies being

[1] See Folin : *Loc. cit.*

[2] See the note by Nef : This JOURNAL, **18**, 753 (1896).

[3] See, the first paper, *Loc. cit.*

used for both (I.) and (II.), acid dehydrating reagents for (II'.), and essentially heat only for (III.). It is the intermediate product, such as $RCO.N=$,[1] which is considered to suffer the molecular rearrangement proper, owing to the potency of the free valences of univalent nitrogen. For instance

$$OC—N \quad \longrightarrow \quad OC—NR \quad \longrightarrow \quad OC = NR$$
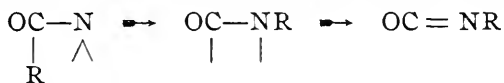
an isocyanate is formed in this case as the first tangible product.[2]

According to this interpretation, the rearrangement should not be possible if, for instance, in the acid bromides the loss of hydrobromic acid is prevented by replacing the hydrogen atom by an alkyl or an alphyl group. The work with Mr. Slosson has proved that such is actually the case, neither series of derivatives of the acid bromides, $RCO(NR'Br)$ and $RC(OR')NBr$, undergoing the change in question. Likewise, it will be remembered, Dr. Higbee found that oximes, $RCO.(NC_6H_5)OH$, which cannot lose water in the way described, show no tendency whatever to undergo the "Beckmann rearrangement." The interpretation is, therefore, in agreement with the three most striking fundamental characteristics of the rearrangement.

It is also in complete accord with the most recently discovered cases of a " Beckmann rearrangement," *viz.*, that of benzylazides, according to[3]

$$C_6H_5CH_2N.(N_2) \quad \longrightarrow \quad C_6H_5CH_2N: +$$
$$N_2 \quad \longrightarrow \quad CH_2 = NC_6H_5 + N_2.$$
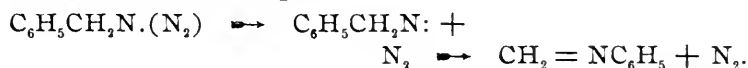
Not one of the other theories proposed can account for this additional instance of a " Beckmann rearrangement."

In further support of the views expressed, the following instances will be mentioned in which the formation of univalent nitrogen derivatives from the classes of compounds under discussion is clearly indicated :

[1] Tiemann, I find, expressed, incidentally, a similar view in regard to one of the above classes of compounds. Ber. d. chem. Ges., **24**, 4163 (1891).

[2] Hofmann: Ber. d. chem. Ges., **15**, 411, 412 (1883). Hantzsch: *Ibid.*, **27**, 1256 (1894). Thiele: Ann. Chem. (Liebig), **309**, 189 (1889). Dr. L. W. Jones, this laboratory, private communication. See Graebe : *Loc. cit.*

[3] Curtius : J. prakt. Chem., **63**, 428 (1901) ; Ber. d. chem. Ges., **35**, 3229 (1902).

Stieglitz.

a. An exhaustive study of the many remarkable reactions of β-phenylhydroxylamine and its homologues has led Bamberger[1] to the conclusion that a phenylimide is the first un-isolated product from which many varied derivatives are obtained. For instance, on heating β-phenylhydroxylamine, azobenzene and water are the chief products of decomposition, a reaction which may be interpreted :

$$C_6H_5NHOH \quad \longrightarrow \quad C_6H_5N= \ + H_2O$$

and

$$2C_6H_5N= \quad \longrightarrow \quad C_6H_5N = NC_6H_5.$$
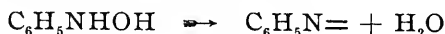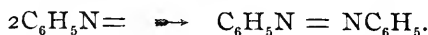
At the same time, the characteristic odor of a carbylamine, $RNC=$, is developed exceedingly strongly. As an ordinary carbylamine can hardly be produced under these circumstances, the suspicion is aroused that the odor is due to small quantities of the analogous phenylimide, $C_6H_5N=$, escaping instantaneous condensation.[2]
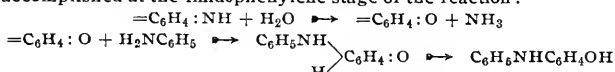
[1] Ber. d. chem. Ges., **27**, 1550 (1894) ; **33**, 3600 (1900) ; **34**, 61 (1901).

[2] NOTE.—It seems very probable, however, that phenylimide, as soon as formed, goes over, partly, into the isomeric imidophenylenes :

I.
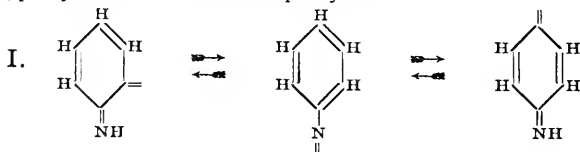
and it remains a question, therefore, to which of these substances the carbylamine odor is really due.

This conception of the partial isomerization of phenylimide seems to me to give a better interpretation than Bamberger's of all of the reactions of phenylhydroxylamine discussed and investigated so brilliantly by Bamberger (*Loc. cit.*), in which the para (or ortho) position of the phenylimide enters into action. It accounts for the great and varied reactivity of the para-position in taking up, additively, many compounds, such as water, alcohols, anilines, phenols, etc. It also explains, readily, one reaction, which even Bamberger found particularly peculiar and difficult to understand (Ber. d. chem. Ges., **34**, 62), namely, the change of phenylhydroxylamine into paraoxydiphenylamine, on being heated with dilute sulphuric acid ; the partial saponification to a phenol derivative which Bamberger could hardly account for, is accomplished at the imidophenylene stage of the reaction :

$$=C_6H_4:NH + H_2O \quad \longrightarrow \quad =C_6H_4:O + NH_3$$
$$=C_6H_4:O + H_2NC_6H_5 \quad \longrightarrow \quad C_6H_5NH$$
$$\underset{H}{\diagdown}C_6H_4:O \quad \longrightarrow \quad C_6H_5NHC_6H_4OH$$

(For the formation of aniline, see Ber. d. chem. Ges., **33**, 3605 and 3617.)

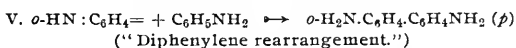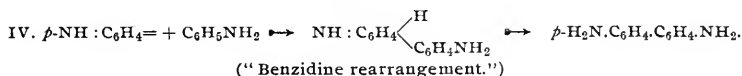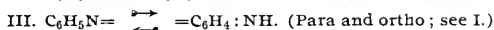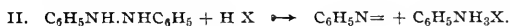It may be added that with the help of Bamberger's fine work and ideas the conception developed here gives us, at last, a complete explanation of the "benzidine rearrangements" of the hydrazines. It is noteworthy that these rearrangements are very easily effected by the agency of even dilute acids, a fact readily understood from the following :

b. Chattaway and Orton[1] have found, likewise, that phenyl-chloramine, C_6H_5NHCl, breaks down readily into hydrochloric acid and azobenzene, and phenylbromamine still more readily into hydrobromic acid and azobenzene.

c. The same chemists[2] and Slosson[3] have found that benzoyl-phenylchloramine, $C_6H_5CO.N(C_6H_5)Cl$, gives, on being heated, some benzoyl chloride[4] (besides forming chiefly *p*-chlorbenz-anilide). In this connection, it is interesting to note that the action of aqueous alkali on the acylalphylhalogen amines, $RCON(C_6H_5)Cl$, while producing an acylanilide as the chief product, was invariably observed by Slosson and myself to be accompanied by the formation of an unknown compound with the pungent carbylamine odor.[5]

d. By the action of phosphorus pentachloride on β-benzoyl-β-phenylhydroxylamine, $C_6H_5CO.N(C_6H_5)OH$, Dr. Higbee has found that some benzoyl chloride is formed and again the inevitable carbylamine odor was most pronounced. Treat-ment of the same substance with acetic anhydride likewise produced this characteristic odor.

e. The reduction products of the acylazides also indicate

II. $C_6H_5NH.NHC_6H_5 + H X \longrightarrow C_6H_5N= + C_6H_5NH_3X.$

III. $C_6H_5N= \underset{\longleftarrow}{\overset{\longrightarrow}{}} =C_6H_4:NH.$ (Para and ortho; see I.)

IV. $p\text{-}NH:C_6H_4= + C_6H_5NH_2 \longrightarrow NH:C_6H_4\big\langle{\overset{H}{\underset{C_6H_4NH_2}{}}} \longrightarrow p\text{-}H_2N.C_6H_4.C_6H_4.NH_2.$

("Benzidine rearrangement.")

V. $o\text{-}HN:C_6H_4= + C_6H_5NH_2 \longrightarrow o\text{-}H_2N.C_6H_4.C_6H_4NH_2 (p)$

("Diphenylene rearrangement.")

VI. $NH:C_6H_4 + H_2NC_6H_5= \longrightarrow HN:C_6H_4\big\langle{\overset{H}{\underset{NHC_6H_5}{}}} \longrightarrow H_2N.C_6H_4NHC_6H_5.$

("Semidine rearrangement.")

VII. $2C_6H_5N= \longrightarrow C_6H_5N:NC_6H_5.$ (Azobenzene formation.)
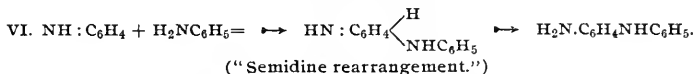
We find, thus, all the interesting products of this important action fully accounted for. These simple interpretations give us a further instance of the usefulness of the conceptions of univalent nitrogen derivatives as intermediate products in molecu-lar rearrangements whose explanation has always proved so baffling to chemists.

[1] J. Chem. Soc. (London), **79**, 462 (1901). Similar cases are described in the same paper.

[2] *Ibid.*, **75**, 1053 (1899).

[3] *Loc. cit.*

[4] The nature of the corresponding nitrogenous dissociation-product has not been determined, as yet. The reaction will be studied further.

[5] Slosson : *Loc. cit.*

an intermediate formation of the elusive univalent nitrogen derivatives.[1]

f. Curtius[2] deduces the formation of the main decomposition products of benzylazide from the rearrangement of benzylimide, $C_6H_5CH_2N=$.

In the first paper on the "Beckmann rearrangement," mention was made of the fact that no determination had been made of the constitution of the metal salts of the acid halogen amides which are formed before the rearrangement is effected.[3] The two forms, $RCO.(NMe\ Hal)$, (I.), and $RC(O\ Me)$ $(N\ Hal)$, (II.), were considered possible. This determination has since been made by Dr. Ransom and myself,[4] and by Hantzsch.[5] Ransom and I have found that diazomethane converts benzchloramide into methyl chlorimidobenzoate,[6] according to

$$C_6H_5CONHCl + CH_2N_2 \longrightarrow C_6H_5C(:NCl)(OCH_3) + N_2.$$

The salts of the acid chloramides, accordingly, have the constitution (II.), corresponding to this ether. We also found that benzchloramide could be titrated quantitatively with a standard alkali, using phenolphthaleïn as the indicator.

A little later, both of these results were also obtained, independently, by Hantzsch; the latter showed by his elegant method of investigation that the free acid halogen amides are not true acids, that the metal derivatives, however, are the salts of true and not very weak acids, and consequently derivatives of a substance of different constitution from the free halogen amides. By analogy to certain corresponding ketones and nitro compounds, Hantzsch assigns to the salts the constitution, (II.), as salts of an unstable hydroxyl acid,

[1] Stieglitz : This JOURNAL, **18**, 753 (1896).

[2] *Loc. cit.*

[3] Stieglitz : *Loc. cit.*

[4] Preliminary note, Ber. d. chem. Ges., **34**, 1615 (1901).

[5] *Ibid.*, **35**, 228 (1902).

[6] The ester was isolated by distillation and characterized by its action on hydriodic acid and on ammonia. By reduction with hydrogen chloride in ligroin solution it gave the hydrochloride of methyl imidobenzoate, $C_6H_5C(NH)OCH_3,HCl$. This salt gave, on being heated, methyl chloride and benzamide, and, on treatment with water, it gave methyl benzoate and ammonium chloride. Finally, treatment of the original chlorimide with hydrogen sulphide and distillation of the product with alkali failed to give even a trace of methylamine, which showed that the isomeric methyl derivative had not been formed even in traces.

RC(OH) (N Hal), to the neutral parent substance the constitution of an amide, RCO.NH Hal. It is evident that the two methods of experimentation, the physico-chemical and the organo-synthetic, supplement each other in a desirable fashion.

This not unexpected result of the determination of the constitution of the salts of the acid bromamides does not affect the interpretation of the " Beckmann rearrangement " as given above ; the change

$$RC(OK):NBr \ \rightarrowtail \ RCO.N: + \ KBr$$
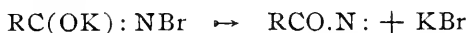
is quite normal in view, notably, of Thiele's[1] work on dissociation and addition reactions involving two even more widely separated atoms in a molecule than are the nitrogen and oxygen atoms in the salts of the acid bromamides.

The constitution of the salts also suggests, however, a loss of potassium bromide and the possible formation of a ring compound, RC : NO, rather than a univalent nitrogen derivative as the intermediate product which actually suffers the molecular rearrangement. The strain in the triatomic ring, rather than the reactivity of univalent nitrogen, would then be the ultimate cause of the rearrangement :

$$C_6H_5C{\underset{O}{\overset{N}{<}}}\Big| \ \rightarrowtail \ CO:NC_6H_5.$$
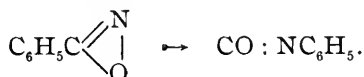
Such a suggestion has been made, incidentally, by Hantzsch[2] in explanation of the rearrangement of the acetate of benzhydroxamic acid, and Baeyer[3] has expressed a similar view in connection with the transformation of ketone peroxides into lactones. It may be said here that such an interpretation could be made even far more general : as the compound, RCO.N=, could very readily go over into the isomeric ring derivative, many of the facts in favor of the formation of the former would obviously hold for the latter. The behavior of the acid bromamides, the hydroxamic acid salts and, possibly,

[1] Ann. Chem. (Liebig), **396**, 87 (1899).
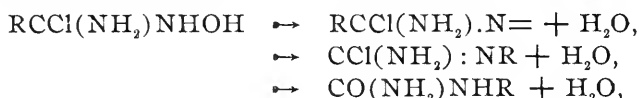[2] Ber. d. chem. Ges., **27**, 1256 (1894). For Hantzsch's most recent views, see note, page 54.
[3] *Ibid.*, **32**, 3627 (1900).

of the acid azides, the contrasting behavior of the substituted acid halogen amides and hydroxamic acids, $RCONC_6H_5(OH)$, would be in equally good agreement with both interpretations. But, after all, the following facts favor decidedly the more comprehensive idea of the agency of univalent nitrogen.

a. Amidoximes, $RC(NOH)NH_2$, undergo the rearrangement[1] under the influence of acid dehydrating reagents as do other oximes. An intermediate ring compound, $RC = N—NH$, an isodiazomethane, and a hydrazine would tend to give hydrazine[2] or to change, if at all, into its closely related isomer, a diazo methane, $RCH—N = N$, and give the latter's decomposition products, nitrogen and an alkylidene derivative, rather than suffer a separation of two carbon atoms from each other, and two nitrogen atoms from each other, against their well-known tendencies. On the other hand, the reactions

$$RCCl(NH_2)NHOH \;\longmapsto\; RCCl(NH_2).N= \;+\; H_2O,$$
$$\longmapsto\; CCl(NH_2):NR \;+\; H_2O,$$
$$\longmapsto\; CO(NH_2)NHR \;+\; H_2O,$$

introduce no new assumption into the theory of the activity of univalent nitrogen—they appear as entirely normal.

b. The ring theory cannot be applied to the rearrangement of the ketoximes until an N-alkyl (alphyl) aldoxime or ketoxime, $R_2C.NR'—O$, has been made to suffer a "Beckmann rearrangement" with a migration of an *alkyl* or an *alphyl* group, R, since such a ring $R_2C—NH—O$ would have to be the cause of the rearrangement of the ketoximes.[3] Such a migration does not appear on record, although the "Beckmann reagents" have been applied to such oximes.[4]

c. According to Werner,[5] the hydroximic acid chlorides,

[1] Tiemann : Ber. d. chem. Ges., **24**, 4162 (1891).

[2] See, Hantzsch : *Ibid.*, **34**, 2507 (1901).

[3] See, Baeyer : *Loc. cit.*

[4] *e. g.*, Beckmann : *Ibid.*, **26**, 2272 (1893).

[5] *Ibid.*, **32**, 1654, 1975 (1899). See these papers for the actual condensation-products.

RCCl(NOH), and benzoates, $RC(O.OCC_6H_5)(: NOH)$, in which the ready formation of the above ring appears particularly well favored, do lose acid easily but no rearrangement ensues.

d. The ring theory is utterly incompatible with the most recent case of a " Beckmann rearrangement," that of benzylazide,[1] $C_6H_5CH_2N(N_2)$, while it appears as a perfectly normal case of a rearrangement of a univalent nitrogen derivative, benzylimide :

$$C_6H_5CH_2N : \quad \rightarrow \quad CH_2 : NC_6H_5.$$
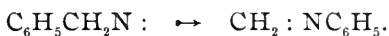
Finally, attention is called, once more, to the fact that, whereas there is not a single fact concerning the constitution and reactions of organic compounds known to the author which does not agree perfectly with the theory of the " Beckmann rearrangement" postulating the intermediate formation of a univalent nitrogen derivative, it does not agree so well with the more obscure relations of the theory of stereoisomerism of ketoximes and their influence on the rearrangement of these isomers.[2] It is hoped that future work will remove this difficulty.

The conclusions arrived at may be summed up as follows :

1. The interpretations of the " Beckmann rearrangement" given by Hoogewerff and van Dorp, Hantzsch, Beckmann, Hesse, Freundler, and Nef do not agree with all the facts established in connection with this reaction.

2. All the most important results of the investigations of the reaction from the point of view of the constitutions of the substances involved agree best with that interpretation which postulates the intermediate formation of a univalent nitrogen derivative as the essential cause of this characteristic rearrangement. This conception is comprehensive enough to satisfy all the cases where the rearrangement has been observed actually to occur in widely varied classes of compounds, such as :

[1] Curtius : *Loc. cit.*
[2] See the first paper, *Loc. cit.*

I.	Acid halogen amides:	$RCONH(Hal)$;
II.	Acyloximido acid salts:	$RC(NOAcyl)(OMe)$;
III.	Ketoximes:	$R_2C(NOH)$;
IV.	Oximido acid esters:	$RC(NOH)(OR)$;
V.	Oximido acids:	$RCO.NHOH$;
VI.	Amidoximes:	$RC(NOH)NH_2$;
VII.	Acid azides:	$RCO.N(N_2)$;
VIII.	Benzylazides:	$RCH_2N(N_2)$.

It also satisfies those otherwise analogous cases where the rearrangement, for no other apparent reason than the impossibility of the fulfilment of this condition, could not be effected, such as:

I'.	Acylalkyl (alphyl) halogen amines:	$RCO(NHal R')$;
II'.	Halogen imido esters:	$RC(NHal)OR'$;
III'.	Acyl-β-alphylhydroxylamines:	$RCO(NR'OH)$;
IV'.	N-Alkyl (alphyl) ketoximes:	$R_2C(NR'O)$.

3. Whatever interpretation be given of the rearrangement, it seems to have been satisfactorily established that the groups of compounds I. and II. suffer the transformation only when opportunity is offered for the loss of the acids, $H(Hal)$ or $HO(Acyl)$, by the formation of their salts, groups III., IV., V., and VI. when dehydrating reagents are used, VII. when nitrogen is evolved under the influence of heat.

CHICAGO, Oct. 13, 1902.

ON BORATE OF MANGANESE.

BY H. ENDEMANN AND JOHN W. PAISLEY.

Borate of manganese is an article of commerce which is used to quite an extent as a dryer for oils, and one would suppose that the substances sold under such designation would possess a certain uniformity of composition.

As a result of a number of analyses of such commercial articles it was learned that this is not so. The substance which acts as the dryer in this compound is the manganous oxide, which dissolves in the oil, while the boric acid acts merely as a protector of this manganous oxide, preventing its oxidation to manganic oxide, which is not wanted for the reason that it induces oxidation of the oil before it is exposed to the air.

No formula for borate of manganese has been published for the reason that it has not been obtained in a pure state, for water used to remove the salts of the mother-liquor removes not only these but also boric acid and manganese, but mainly the former,[1] with the result that compounds remain which do not contain as much boric acid as would correspond to the supposed formula MnB_4O_7. As the boric acid is removed from the precipitate it commences, even during the washing, to turn brown in the air, owing to the oxidation of the manganous oxide, and if not then, certainly on drying even at the ordinary temperature. To prevent this, manufacturers have employed various means. Some use an excess of borax above that required by the equation

$$MnCl_2 + Na_2B_4O_7 = MnB_4O_7 + 2NaCl,$$

and then do not even wash. They sell, practically, a mixture of chloride of manganese and borax. Others wash, and as the product turns brown, restore the color by the addition of sulphite of soda.

Others again wash and supply the loss of boric acid by the admixture of organic acids. The proper proportion is 71 manganous acid to 139.6 boric acid. Such a compound can be dried in air and heated to 150° C. without changing its color, while all which contain less boric acid will turn brown on drying, especially so at an elevated temperature.

With the foregoing as a guide, the composition of borate of manganese, as it is found in trade, can be understood. The samples examined were partly domestic, partly imported. They contain, according to analysis :

	Boric oxide, B_2O_3.	Manganous oxide, MnO.
1	39.36	12.00
2	40.88	16.19
3	37.38	31.06
4	11.09	6.43

Nos. 1 and 2 contained nearly all the salts produced by the reaction, together with an excess of borax. No. 3 was well washed but had sulphite of soda added to restore the color,

[1] Joulin : Ann. chim. phys. [4], **30**, 272.

which sulphite was partially oxidized to sulphate. No. 4 contained a considerable amount of organic resin acids. We will hardly be able to find another product of chemical industry, where, under the same name, substances of such wide divergence in composition are sold.

The question now arose, What is the composition of borate of manganese, which will stand access of air and drying without becoming liable to oxidation? In a recent controversy it was claimed that the composition of borate of manganese, as obtained by precipitation, was $MnO.B_4O_6$, and that the pure article should contain, therefore, 33.7 per cent of manganous oxide and 66.3 per cent of boric oxide. As authority for this we were referred to an article by Prof. Edgar F. Smith, which originally was published in this JOURNAL.[1] We did not find in this publication any analysis of the precipitate referred to. In fact, Prof. Smith had utilized the fact that a 50 per cent alcoholic solution of borax precipitates exactly so much manganese as corresponds to the sodium contained in borax, or, in other words, the sodium contained in borax acts as so much sodium hydroxide under the conditions of the experiment. That the precipitate is not $MnO.B_4O_6$ is evident alone from the fact that it turns brown in the air, which is a certain sign that dissociation had taken place.

By working in an alcoholic solution Prof. Smith had guarded against a loss of manganese, which is an essential condition in his case, but the conditions differ when the precipitation is accomplished in water solution.

While alcohol causes dissociation whereby the precipitate loses boric acid but none of its manganese, water produces dissociation into free boric acid, which is a solvent for the precipitated borate of manganese. We lose, therefore, boric acid as well as manganese. The presence of salts in the mother-liquor causes, likewise, a considerable loss, and among such salts the sulphates are better solvents than the chlorides. For this reason it is better to use chloride of manganese than sulphate of manganese. Sulphate of magnesium, sulphate of manganese, and sulphate of sodium dissolve borate of

[1] This JOURNAL, **4,** 279 (1882).

manganese forming solutions which possess an intensely alkaline reaction towards litmus paper. This solvent action is so great that, using sulphate, but 54 per cent washed precipitate was obtained against 68 per cent in the case of chloride. When borate of manganese is treated with water and the solution examined we find that the proportion of the respective substances is $MnO : 3B_2O_3$. Hence the precipitates become richer in manganese and poorer in boric acid.

Of the many analyses made of such washed precipitates we give the following :

I. is obtained by precipitating equivalent quantities of sulphate of manganese and borax.

II. is obtained by using a slight excess of sulphate of manganese.

The loss on heating is mainly water, always increased, however, by the loss of some boric acid carried off by the water.

	I.	II.
Loss on heating	30.90	31.57
MnO	26.78	28.82
B_2O_3	42.36	39.69

To correspond to the formula $MnO.B_4O_6$, I. should have contained for the manganese present 52.8, and II. 56.8 per cent of boric acid. This is irrespective of the water always contained in the product and which in the pure salt is $5H_2O$. At one time it was thought possible that the loss of boric acid could be obviated by washing the precipitate with a saturated solution of boric acid in water, and even prepare the respective solutions of manganous chloride and borax with a saturated solution of boric acid, but this treatment was followed only by a considerable loss of precipitate without changing the composition to any extent.

Since the precipitation takes place in water, the precipitate has never the composition which might be expected from the reaction above referred to. The precipitate has then already suffered from dissociation, as I ascertained by removing the water and with it the salts as far as mechanical means allow, entirely avoiding washing, however, and then analyzing not

only the precipitate but the solution likewise. This takes place even when we try to produce a precipitate which contains 1 molecule of MnO for 1 molecule of B_2O_3, though not so marked ; *i. e.*, dissociation decreases as the manganese increases in the precipitate, and this may be washed even without much loss of boric acid and hardly any loss of manganese. This precipitate keeps white while wet but darkens on drying.

There is but one product which possesses sufficient stability, and this is $MnO.B_4O_6 + 5H_2O$, which, however, may not be produced directly by precipitation. It can, however, be obtained by adding so much boric acid to wet precipitates, lacking boric acid, as the theory demands, and then allowing to dry spontaneously. Such mixtures dry white (rose) and remain so when dried even as high as 150° C. They are absolutely amorphous, which would not have been the case if the boric acid had not gone into combination. Even the microscope does not reveal any crystals. Heating with a little water in a sealed tube produces a granular mass. The formula of this compound is $MnB_4O_7 + 5H_2O$. At 120° C. it loses $2H_2O$.

Loss at 120° C.	Calculated.	Found.
$2H_2O$	11.98	12.04

The salt, however, is quite hygroscopic and should therefore be well dried over sulphuric acid under the air-pump. At temperatures above 120° C. the salt loses water gradually, but the rest of the water can be removed only at red heat, when some boric acid is also lost by being carried off by the water. The salt, therefore, colors by oxidation. It is quite dense and is evidently not well suited to be applied technically.

The salt $MnB_4O_7 + 3H_2O$, when finely ground and brought into contact with water, takes up again $2H_2O$, lost on drying, setting thereby like plaster of Paris.

Both hydrated salts yield their manganese readily to hot oils, producing quick-drying varnishes. The most convenient and economical method for the production of the salt consists in precipitating a borate of manganese of the approximate

composition, MnB_2O_4, using a solution of manganese chloride and a borax solution to which so much sodium hydroxide has been added as the borax already contains, then filtering, and washing rapidly with cold water free from air. In the solution the boric acid and manganese are determined, and from this it is easily possible to calculate the quantity of boric acid which should be added to the mass remaining upon the filter. Working under the same conditions, I should think that manufacturers, once for all, could determine such quantity of acid, especially as a slight excess of boric acid does not influence the nature of the dryers.
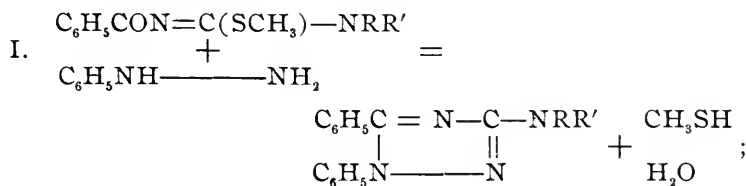
The analytical work is not onerous, since caustic soda decomposes the salt easily into manganous hydroxide and borate of sodium. The manganese in the precipitate is determined volumetrically by Volhard's method, while the boric acid is determined in the solution by means of the glycero-boric acid method.
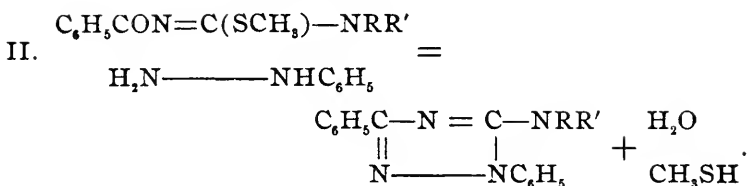
―――

C. — ON THE ACTION OF PHENYLHYDRAZINE ON BENZOYLPSEUDOTHIOUREAS : 1,5-DI-PHENYL-3-AMINOPYRRO-α,β'-DIA-ZOLE DERIVATIVES.

BY HENRY L. WHEELER AND ALLING P. BEARDSLEY.

It was stated in a previous article[1] that the acylpseudothioureas readily react with phenylhydrazine to form aminotriazoles, but the question whether the resulting aminotriazoles are 1,5-dialkyl-3-aminotriazoles (formula I.) or 1,3-dialkyl-5-amino derivatives (formula II.) was not decided at that time.

I. $$\begin{array}{c} C_6H_5CON{=}C(SCH_3){-}NRR' \\ + \\ C_6H_5NH\text{―――}NH_2 \end{array} = \begin{array}{c} C_6H_5C = N{-}C{-}NRR' \\ | \quad\quad || \\ C_6H_5N\text{―――}N \end{array} + \begin{array}{c} CH_3SH \\ + \\ H_2O \end{array} ;$$

[1] This JOURNAL, **26**, 411 (1901).

II.
$$\frac{C_6H_5CON=C(SCH_3)-NRR'}{H_2N\text{------}NHC_6H_5} =$$

$$\begin{array}{c} C_6H_5C-N = C-NRR' \\ \parallel \qquad\quad | \\ N\text{------}NC_6H_5 \end{array} + \begin{array}{c} H_2O \\ \\ CH_3SH \end{array}.$$

It was shown that certain acylcarbamic, acylthiocarbamic, and acylimidothiocarbonic esters act with phenylhydrazine, forming triazole derivatives, and in these cases the relative tendency of the groups to react with the hydrogen of the amino group in phenylhydrazine could be expressed by the following arrangement :
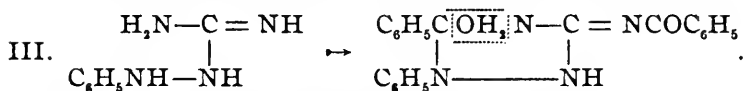
$$CSAlk > CS > CO > COAlk.$$
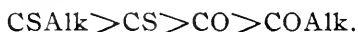
That is to say, mercaptan is eliminated rather than hydrogen sulphide, and both these products more readily than water or alcohol, the latter appearing to have the least tendency to separate.[1]   From this it would be expected that the triazoles formed from the benzoylpseudothioureas would be 1,5-diphenyl-3-aminotriazoles, the reaction taking place according to the first equation.   This we have proved to be the case, as follows :

(*a*) When the product obtained from benzoylthiolmethyl-pseudothiourea, $C_6H_5CON = C(SCH_3)NH_2$, and phenylhydrazine was acted on by nitrous acid in concentrated hydrochloric acid, the amino group was replaced by chlorine, and the resulting compound appeared to be identical with the chlortriazole obtained by Cleve[2] from 1,5-diphenyloxytriazole. Cleve states that the chlorine derivative melts at 96°, while our product melted at 95° to 95°.5.

(*b*) The substance was shown conclusively to be a 1,5-diphenyltriazole by the following synthesis :   Phenylamino-guanidine, in ether, was shaken with benzoyl chloride and alkali.   This produced a dibenzoyl derivative which, on boiling in alcohol, separated water and gave 1,5-diphenyl-3-benzoylaminotriazole (III.) :
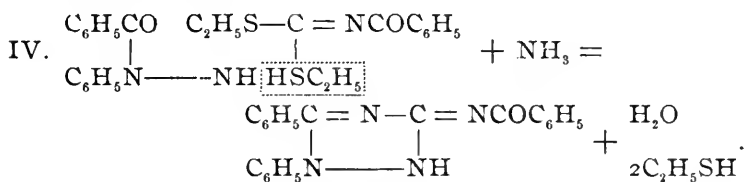
[1] This JOURNAL, **27**, 258 (1902).
[2] Ber. d. chem. Ges., **29**, 2672.

$$\text{III.} \quad \begin{array}{c} H_2N-C = NH \\ | \\ C_6H_5NH-NH \end{array} \quad \longmapsto \quad \begin{array}{c} C_6H_5C[OH_2]N-C = NCOC_6H_5 \\ | \qquad\qquad | \\ C_6H_5N\text{———}NH \end{array}.$$
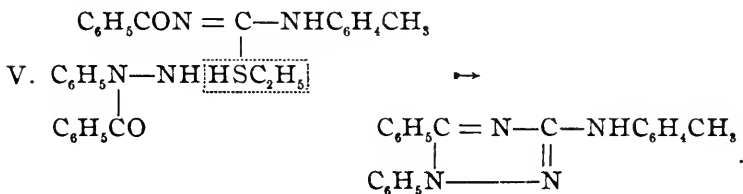
When this benzoyl derivative was saponified, the resulting aminotriazole proved to be identical with the aminotriazole from the acylpseudothiourea and phenylhydrazine.

(*c*) The same benzoylaminotriazole was obtained from our aminotriazole and benzoyl chloride, and also by causing unsymmetrical benzoylphenylhydrazine to act on benzoyliminodiethyldithiocarbonate, and then boiling the resulting *a*-phenyl-*a,c*-dibenzoylthiolethylpseudothiosemicarbazide (IV.) with alcoholic ammonia.

$$\text{IV.} \quad \begin{array}{c} C_6H_5CO \quad C_2H_5S-C = NCOC_6H_5 \\ | \qquad\qquad | \\ C_6H_5N\text{——}NH[HSC_2H_5] \end{array} + NH_3 =$$

$$\begin{array}{c} C_6H_5C = N-C = NCOC_6H_5 \\ | \qquad\qquad | \\ C_6H_5N\text{———}NH \end{array} + \begin{array}{c} H_2O \\ + \\ 2C_2H_5SH \end{array}.$$

That the same reaction by which the aminotriazole is obtained from phenylhydrazine and the above benzoylpseudothiourea holds equally for the production of substituted aminotriazoles from substituted pseudothioureas, was proved by preparing the paratolyl derivative by the following method: Benzoylparatolylthiolethylpseudothiourea was warmed with unsymmetrical benzoylphenylhydrazine, whereupon mercaptan was eliminated and *a,c*-dibenzoyl-*c'*-paratolyl-*a*-phenylaminoguanidine (V.) was formed. When this was boiled with the calculated quantity of dilute alcoholic potash a benzoyl group was removed and water was split off, yielding 1,5-diphenyl-3-paratolylaminotriazole. This compound was found to be identical with the product obtained by Wheeler and Johnson from benzoylparatolylthiolethylpseudothiourea and phenylhydrazine.

$$\text{V.} \quad \begin{array}{c} C_6H_5CON = C-NHC_6H_4CH_3 \\ | \\ C_6H_5N-NH[HSC_2H_5] \\ | \\ C_6H_5CO \end{array} \quad \longmapsto$$

$$\begin{array}{c} C_6H_5C = N-C-NHC_6H_4CH_3 \\ | \qquad\quad || \\ C_6H_5N\text{———}N \end{array}.$$

As far as examined, the acylpseudothioureas conform to the rule above mentioned. The —NH$_2$ group of the phenylhydrazine attacks the mercapto group in preference to the CO group. The question whether the above rule applies in the case of other types of compounds that contain these groups, and give triazoles[1] or their analogues, will receive attention at a later time.

<div align="center">EXPERIMENTAL PART.</div>

Benzoylthiolbenzylpseudothiourea,

C$_6$H$_5$CO—N $=$ C(SCH$_2$C$_6$H$_5$)NH$_2$.—Benzoylthiourea was dissolved in dilute potassium hydroxide and benzyl chloride was added, the mixture being subjected to violent agitation by a mechanical stirrer. After filtering, the resulting semisolid mass was crystallized from alcohol, whereupon it formed glistening white plates, insoluble in ether or benzene. It was soluble in hydrochloric acid and it melted at 161°. A nitrogen determination gave :

	Calculated for C$_{15}$H$_{14}$ON$_2$S.	Found.
N	10.37	9.94

1,5-Diphenyl-3-aminotriazole. — Molecular proportions of phenylhydrazine and benzoylthiolmethylpseudothiourea[2], or the above pseudothiourea, were heated on the water-bath, in benzene, for three or four hours. After the benzene had been evaporated the reaction-product was washed with ether and crystallized from alcohol. It formed colorless prisms, which melted at 154°.5. A nitrogen determination gave the following result :

	Calculated for C$_{14}$H$_{12}$N$_4$.	Found.
N	23.72	23.71

This aminotriazole is very difficultly soluble in water and cold benzene, readily in hot benzene and alcohol. From the latter solvent it separates in the form of prisms or striated plates. It is very stable, strong, boiling sulphuric acid or

---

[1] Certain acylphenylthioureas and acylphenylurethanes cannot be used to test this rule since they react abnormally, saponification taking place. J. Am. Chem. Soc., **22,** 368 (1900).

[2] Wheeler and Merriam : *Ibid.,* **23,** 293 (1901).

potash having no effect on the substance. Attempts to prepare the substance by heating 1,5-diphenyl-3-chlortriazole[1] or the mercaptotriazole, or the alkylmercaptotriazoles[2] with ammonia were without success.

It behaves in a manner peculiar to the aminotriazoles on attempting to diazotize in hydrochloric acid solution. The base was dissolved in concentrated hydrochloric acid and to the cold solution the calculated quantity of sodium nitrite was added. After the mixture had stood for several hours at 0°, crystals separated which, on purification by alcohol, melted at 95° to 95°.5 and appeared to be identical with the 1,5-diphenyl-3-chlortriazole described by Cleve.[3] A nitrogen determination gave :

	Calculated for $C_{14}H_{10}N_3Cl$	Found.
N	16.43	16.42

The *picrate* forms intensely yellow, lozenge-shaped plates, on mixing alcoholic solutions of the constituents. It melts at 183°. A nitrogen determination gave :

	Calculated for $C_{20}H_{15}O_7N_7$.	Found.
N	21.11	21.43

The *hydrochloride* results when the aminotriazole is boiled in concentrated hydrochloric acid. On cooling, small, colorless plates separate, which melt at 205°, without effervescence, being distinguished by this from the benzoyl chloride addition-product, which melts at the same point, but with effervescence. A nitrogen determination gave :

	Calculated for $C_{14}H_{13}N_4Cl$.	Found.
N	20.55	20.52

1,5-Diphenyl-3-benzoylaminotriazole.—This was prepared by adding benzoyl chloride (1 molecule) to the aminotriazole (2 molecules) in warm benzene. Under these conditions the above hydrochloride separates and the benzoyl derivative remains in solution.

[1] Cleve : Ber. d. chem. Ges., **29**, 2672.
[2] This JOURNAL, **27**, 257 (1902).
[3] *Loc. cit.*

It can also be obtained from the benzoyl chloride addition-product, either by shaking with alkali and dissolving out the product with benzene, or by heating the substance to its melting-point, when hydrogen chloride is evolved, leaving the benzoyl derivative as a brittle resin. This crystallizes from dilute alcohol or from benzene and ligroin, and melts at 159° to 160°. A nitrogen determination gave :

	Calculated for $C_{21}H_{16}ON_4$.	Found.
N	16.47	16.39

Benzoylaminotriazole is readily soluble in benzene and alcohol. It is precipitated from its alcoholic solution by water. On evaporating its solutions on the steam-bath it forms a varnish. When treated with hydrochloric acid it is converted into a hydrochloride. This is identical with the benzoyl chloride addition-product described below.

The *sulphate* is produced when its alcoholic solution is allowed to evaporate at ordinary temperatures with dilute sulphuric acid. The resulting crystals, purified by dissolving in alcohol and precipitating with ether, melted at 195°.

The Hydrochloride or Benzoyl Chloride Addition-product.— When the aminotriazole was warmed in an excess of benzoyl chloride without a solvent, on the steam-bath, it dissolved and then suddenly precipitated out as a solid cake. This was washed with benzene, in which it is insoluble, and crystallized from alcohol. It formed bunches of small, colorless plates, which melted at 205° with effervescence. A nitrogen determination gave :

	Calculated for $C_{21}H_{17}ON_4Cl$.	Found.
N	14.87	15.07

1,5-Diphenyl-3-acetylaminotriazole Hydrochloride. — When acetyl chloride was added to the aminotriazole, vigorous action took place. A viscous paste was immediately formed, which was gradually changed to a white powder by boiling with the chloride. This, on washing with benzene, melted at 156° to 157°, and was analyzed with the following result :

	Calculated for $C_{16}H_{16}ON_4Cl$.	Found.
N	17.80	17.71

The constitution of the triazole derivatives just described was determined by the two following syntheses :

I. a,c-Dibenzoyl-a-phenylaminoguanidine, $C_6H_5N(COC_6H_5)$— NH—$C(NH)$—$NHCOC_6H_5$.—P h e n y l a m i n o guanidine[1] (6 grams) and benzoyl chloride were added to 200 cc. of dilute sodium hydroxide, covered with ether, with vigorous shaking. As soon as an excess of benzoyl chloride was evident from its odor, the precipitate was filtered and washed with water and ether. The yield was 8.5 grams. This material could not be crystallized unaltered from alcohol. As obtained above, possessing every appearance of purity, it melted with effervescence at 156°, and a nitrogen determination gave :

	Calculated for $C_{21}H_{18}O_2N_4$.	Found.
N	15.64	15.50

When this compound was boiled for six hours in absolute alcohol, it was dehydrated, 1,5-diphenyl-3-benzoylaminotriazole resulting. To the alcoholic solution of the last, strong hydrochloric acid was added and the boiling continued. The benzoyl group was thus removed and the hydrochloride of 1,5-diphenyl-3-aminoguanidine formed, from which the free base was obtained by alkali. This product and that from the action of phenylhydrazine on the benzoylpseudothioureas were identical.

II. a-Phenyl-a,c-dibenzoylthiolethylpseudothiosemicarbazide, $C_6H_5N(COC_6H_5)NH$—$C(SC_2H_5)$=$NCOC_6H_5$. — W h e n 4 grams of *a*-benzoyl-*a*-phenylhydrazine and 4 grams of benzoylimidodithiodiethyl carbonate[2] were warmed in alcohol, mercaptan was evolved. Evaporation of the alcohol left a varnish which crystallized from benzene in square plates, melting at 170° to 171°. When pure it is difficultly soluble in alcohol. A nitrogen determination gave :

[1] Pellizzari: Gaz. chim. ital., **21**, 333.

[2] This compound and the analogous imidodimethyl carbonate were described as carbamates, owing to a typographical error in the manuscript. J. Am. Chem. Soc., **23**, 292 (1901).

	Calculated for $C_{23}H_{21}O_2N_3S$.	Found.
N	10.42	10.37

This material was boiled with alcoholic ammonia, where-upon it very slowly dissolved and mercaptan was evolved, and there was formed, as an intermediate product, *a*-phenyl-*a,c*-dibenzoylaminoguanidine. The latter, however, under the conditions of the experiment, eliminated water, becoming 1,5-diphenyl-3-benzoylaminotriazole. Hydrogen chloride was passed into the benzene solution and the precipitate thus produced was crystallized from alcohol and proved identical with the benzoyl chloride addition-product described above.

1,5-Diphenyl-3-phenylaminotriazole.—This was prepared by warming benzoylphenylthiolethylpseudothiourea,

$$C_6H_5CONHC(SC_2H_5) = NC_6H_5,^1$$

on the steam-bath with the molecular proportion of phenylhydrazine. After three or four hours' heating, mercaptan had ceased coming off and the product had solidified. The residue was crystallized from alcohol from which it appears in fine, white needles, melting at 202°. A nitrogen determination gave :

	Calculated for $C_{20}H_{16}N_4$.	Found.
N	17.94	17.99

Phenylaminotriazole does not form a hydrochloride, either when treated with hydrochloric acid or when hydrogen chloride is passed into its solution in benzene. It may be boiled for hours with strong alkali with no effect. It could not be prepared from the chlortriazole or the mercaptotriazoles by heating with aniline.

1,5-Diphenyl-3-benzoylphenylaminotriazole is formed when phenylaminotriazole is heated with benzoyl chloride on the water-bath. The reaction-product, crystallized from dilute alcohol, appears in compact, ill-formed crystals, which are very soluble in benzene and insoluble in ligroin. It was found to melt at 148° to 149° and a nitrogen determination gave :

---

[1] J. Am. Chem. Soc., **23**, 293 (1901).

	Calculated for $C_{27}H_{20}ON_4$.	Found.
N	13.46	13.60

1,5-Diphenyl-3-paratolylaminotriazole.—This has been prepared by Wheeler and Johnson[1] from benzoylparatolylthiolethylpseudothiourea and phenylhydrazine. The following process leads to the same compound : Molecular quantities of *a*-benzoyl-*a*-phenylhydrazine and benzoylparatolylthiolethylpseudothiourea were warmed in alcohol on the steam-bath. Mercaptan came off slowly and after long heating the material solidified. It was difficultly soluble in alcohol, and formed long, colorless needles which melted at 279° with effervescence. The material was free from sulphur, and a nitrogen determination agreed with the calculated for *a,c*-dibenzoyl-*c'*-paratolyl-*a*-phenylaminoguanidine :

	Calculated for $C_{28}H_{24}O_2N_4$.	Found.
N	12.5	12.8

This substance was boiled with dilute alcoholic potash, whereupon, in about a half hour, beautiful, colorless, minute, stout crystals separated which melted at 227° to 228°. This material proved identical with the paratolylaminotriazole previously prepared, but to which the melting-point 225° to 226° was assigned.

Benzoylmethylphenylthiolmethylpseudothiourea,
$C_6H_5CON = C(SCH_3)NCH_3C_6H_5$. — Molecular quantities of benzoylimidodithiodimethyl carbonate and monomethylaniline were heated in benzene, on the water-bath, for three or four hours. After evaporating the benzene the product was washed with ether and crystallized from alcohol. It formed colorless prisms melting at 113°. A nitrogen determination gave :

	Calculated for $C_{16}H_{16}ON_2S$.	Found.
N	9.86	9.90

1,5-Diphenyl-3-methylphenylaminotriazole.—Benzoylmethylphenylthiolmethylpseudothiourea was dissolved in a mixture of benzene and alcohol, exactly one molecular proportion of

[1] This JOURNAL, **26**, 414 (1901).

phenylhydrazine added, and the mixture allowed to stand in the cold. After several days a few crystals had separated. The mother-liquor was found to contain only unaltered material. The crystals were purified by alcohol, in which they are extremely insoluble. They formed lozenge-shaped plates which melted with effervescence at 202° to 203°, after showing signs about 5° lower. The material was free from sulphur, and nitrogen determinations gave the following results :

	Calculated for $C_{21}H_{18}N_4$.	I.	II.
		Found.
N	17.18	16.84	16.89

NEW HAVEN, CONN., Nov., 1902.

SEPARATION OF LEAD FROM MANGANESE BY ELECTROLYSIS.

BY A. F. LINN.

In its chemical properties manganese very closely resembles iron, but on electrolysis it behaves more like lead. Neumann[1] has described a method for the separation of lead and manganese, by the current, in the presence of 20 per cent of free nitric acid, at a temperature between 60° and 70° C. The current density was 1.5 to 2 amperes and the electromotive force 2.5 to 2.7 volts. The method yields only approximately accurate results when carried out as described, and when the amount of manganese does not exceed 0.03 gram for 150 cc. of the electrolyte. If the amount of manganese exceeds 0.03 gram, or if the deposition continues too long, the lead peroxide deposit is no longer free from the other metal. In a former paper[2] I have shown that lead can be completely deposited from a solution of its phosphate in an excess of phosphoric acid. The similarity of lead to manganese, referred to above, led me to try the current on a manganese solution under like conditions. No deposit whatever was obtained, even after prolonged action of the current. The solution, however, acquired the pink color usually produced in acid solutions of manganese, and mentioned by Neumann[3] and also by

---

[1] Chem. Ztg., 1896, No. 39, p. 20.
[2] J. Am. Chem. Soc., **24**, 435.
[3] " Electrolytic methods of analysis."

Experimental Results.

No.	Lead taken. Gram.	Lead found. Gram.	Difference. Per cent.	$N.\,D._{100}$. Ampere.	Voltage.	Hours.	Dilution. cc.	H_3PO_4. cc.	Manganese. Gram.
1	0.1000	0.1001	+0.10	0.005	2.75	22	130	13	0.05
2	0.1000	0.0998	—0.20	0.004	"	24	"	13	"
3	0.0344	0.0344	....	0.005	2.57	21	"	10	"
4	"	0.0344	....	"	"	17	"	10	"
5	"	0.0343	—0.29	"	2.50	22	"	7	"
6	0.1000	0.0997	—0.30	0.006	2.6	17	"	14	"
7	0.0625	0.0622	—0.48	0.005	"	"	"	10	"
8	0.0750	0.0755	+0.66	"	2.7	"	"	10	"
9	0.0613	0.0618	+0.80	0.003	2.3	"	"	12	"
10	0.1000	0.0998	—0.20	0.005	2.6	18	"	14	0.10

Smith.[1] This difference of deportment toward the current suggested a method of separation. The preliminary trials showed that the lead was completely deposited on the cathode as metal, but that it enclosed a small amount of manganese. Further work has shown that under different conditions a perfect separation is possible. The method of working is similar to that employed when lead alone is present. To a definite amount of lead and manganese, in solution as nitrates, is added sodium hydrogen phosphate, slightly more than sufficient for complete precipitation. The phosphates are then dissolved in an excess of pure phosphoric acid solution (sp. gr. 1.70), and the solution acted on by a current of known strength. The deposit of lead is rapidly washed with cooled, freshly-boiled distilled water, absolute alcohol and ether, dried at 100° to 110° C. in the air-bath, and weighed. The amounts of lead and manganese should not exceed 0.1 gram each for 130 cc. of the electrolyte. The time required for this amount is sixteen to seventeen hours. The time can be shortened by increasing the current density, but in that case the deposit is spongy and seems to be very rapidly soluble in the wash-water. If the lead exceeds 0.1 gram there are apt to be found on the cathode, at certain places, patches of needle-like crystals of lead. All the results recorded above were obtained at ordinary temperatures. Application of heat (60° to 70° C.) retards instead of hastens the deposition of the lead. In each experiment made a small amount of the hydrated peroxide of manganese formed upon the anode. In most instances the color of this deposit was brown, but in a few cases it had a decidedly copper-red appearance.

A portion of this work was carried out in the laboratory of the University of Michigan.

I desire here to acknowledge my indebtedness to Professor Prescott and to Drs. Gomberg, Campbell, and Sullivan for courtesies received.

[1] This JOURNAL, **8**, 208.

REVIEWS.

The important discovery of zymase by Buchner in 1897, together with the remarkably interesting results reached by Fischer in the study of the influence of stereoconfiguration on the action of enzymes, and the important researches of Croft Hill on reversible zymohydrolysis have served to awaken a new interest in the chemistry of zymotic processes during the last few years. Some evidence of this increased activity in this field is furnished by the fact that during the last few years no less than three comprehensive works on this subject have appeared. These are the following : '' The Soluble Ferments and Fermentation,'' by J. Reynolds Green ; '' Die Fermente und ihre Wirkungen,'' by Carl Oppenheimer ; and '' Les Enzymes et leurs Applications,'' by J. Effront. An English translation of this last work is now at hand. The French edition of Effront's book has enjoyed a wide reputation. In its original form the book is divided into two parts. Part I. deals with the enzymes of the carbohydrates, and the oxidases, and their practical application in the industrial arts. Part II. is still in preparation and will have to deal with the proteolytic enzymes and the toxins. It has been the aim of the translator to render '' available in English the valuable material contained in the original French edition.''

Taken as a whole the book, both in the original and in the translation, has much to recommend it to persons interested in the subject of fermentation. It gives us a readable and intelligible account of the enzymes of the carbohydrates and fats, and the oxidases. It treats of their discovery, occurrence, and distribution in nature, the methods of preparation, and their properties. It describes the chemical changes produced by these enzymes and gives the laws and conditions governing their mode of action. Generally speaking, the author inclines to the practical side of the subject, and it is in such portions of the book especially that one finds a great many hints and suggestions of value. About one-fourth of the book is devoted to the consideration of diastase (amylase). At first thought it might seem that too much space had been set apart for the consideration of this enzyme in a work of this size. On the other hand, when we consider the great historical interest attaching to this enzyme, its wide distribution in the vegetable and animal kingdom, its important rôle in

metabolism, and its great application in the brewing industry, it is perhaps not too much after all. The author inclines, and rightly too, I think, to the French nomenclature, first proposed by Duclaux, whereby the enzyme takes the ending ASE, and is named, whenever it is possible to do, after the substance on which its action was first observed. In the main, this system of nomenclature has been adhered to both in the original and in the translation, and yet, in both, the somewhat antiquated name of steapsin for the fat-splitting enzyme is frequently used. The value of the book has been considerably increased by putting the chapter contents at the beginning of each chapter, and by a comprehensive bibliography which, for the sake of convenience, has been subdivided and placed at the end of each chapter, or in some cases at the end of certain general or special topics. In these several bibliographies a decided leaning to the French literature of the subject is observable. If this is a fault it is certainly not an unnatural one in a French author, and in some respects it is a good one, for the reason that he has gotten together in available form all of the more important references to the work of the French school on this subject. On the other hand, the book is no mere compilation. One can easily see that it has been written by a worker and a doer in this field, and after all, this is perhaps its strongest point.

The translation of the work by Prescott has been made in the spirit of the original, and will doubtless prove serviceable to American chemists and physiologists.

It is not intended to convey the idea, however, that either the original or the translation is altogether free from faults and mistakes. Both show typographical errors, for some of which the publishers, for others the author and translator are responsible, and in both the original and the translation there has been observed an occasional looseness and carelessness of expression which tend to confuse the reader and which, with a little pains, could have been avoided. Thus, under the head of Emulsin in the original, page 311, one finds this sentence :

" L'émulsine, qui agit sur des corps très différents au point de vue chimique, agit différemment sur les divers glucoses, d'après leur configuration."

Here the word glucoses is used for glucosides. In the translation this sentence is rendered thus :

" Emulsin, which acts on bodies very differently from a chemical point of view, acts differently on the various monosaccharides, according to their configuration."

It will be observed that the error in the original is repeated

in the translation, and that in addition to this a mistake oc-
curs in the translation itself. Taken together, these two mis-
takes have robbed an important sentence entirely of its mean-
ing. Then again, the constant use of the word diastase as a
general name for enzyme is scarcely warranted by the best
English usage. The word diastase, meaning enzyme, is good
French, but this does not make it good English.

Similarly, the use of the words "hydration" and "hydra-
ting," in lieu of hydrolysis and hydrolyzing, should not be
allowed to pass unnoticed. The processes of hydration and
hydrolysis are altogether different from a chemical point of
view. Both apparently involve the direct union of water and
the substance acted on. In the process of hydration, how-
ever, as this term is ordinarily employed, the action stops at
this point, whereas in hydrolysis a subsequent decomposition
of the complex molecule occurs with the production of one or
more simpler substances. As the enzymes seem to be
primarily concerned in bringing about just such decompositions,
through the agency of water, it would seem better to still
hold to the word hydrolysis, and certainly there is nothing to
be gained in calling the process hydration. These are doubt-
less minor errors, but like the spelling of Fischer's name
Fische in the original, and Bunsen's Bunzen in both the orig-
inal and in the translation, they nevertheless serve to detract
somewhat from the merits of the publication.   J. H. K.

DIE ZEHRSETZUNG STICKSTOFFFREIER ORGANISCHER SUBSTANZEN
    DURCH BAKTERIEN. Von. DR. O. EMMERLING, Privatdozent an der
    Universität Berlin. Mit sieben Lichtdrucktafeln. Braunschweig :
    Druck and Verlag von Friedrich Vieweg und Sohn. 1902. 141 pp.

This little monograph arose from a series of lectures which
the author delivered to chemists on bacterial fermentations.
It is intended to give, briefly, details which cannot be taken up
in the lectures. He first takes up fermentations which result
in oxidation, beginning with the acetic acid fermentation.
The lactic acid fermentation is next considered and attention
is called to its importance in agriculture and in the arts. The
butyric acid and the butyl alcohol fermentations, as well as
the fermentation of cellulose, are also fully considered. The
book contains much information concerning the chemical de-
compositions of nitrogen-free organic matter brought about by
bacteria, and will undoubtedly be of much service to those in-
terested in this field of work. Two excellent methods for the
preparation of lactic acid and dioxyacetone by means of bac-

teria are given by the author, which are not found in any book on organic chemistry. The book contains a good index and seven tables of microphotographs of bacteria. W. R. O.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE UND VERWAND-TER THEILE ANDERER WISSENSCHAFTEN. Begründet von J. LIEBIG und H. KOPP; unter Mitwirkung namhafter Fachgenossen herausgegeben von G. BODLÄNDER, W. KERP, und G. MINUNNI. Für 1894. Viertes Heft. Fünftes Heft. Braunschweig : Vieweg. 1902.

The old Jahresbericht comes slowly along, and it appears to be running a hopeless race. The fourth and fifth numbers for the year 1894 have recently been issued, and will of course be welcome. It would be cruel to complain of the delay in the preparation of this valuable work. The task is almost superhuman, and chemists may be thankful if they get for any year this complete record of the work done by chemists. How the editors and publishers are ever to make up the arrears of eight years it is hard to say. They have been trying to do so for many years past. Editors come and editors go. It is to be hoped that Liebig's Jahresbericht will go on forever. I. R.

Corrections.

As the corrected proof of the article by S. F. Acree and J. E. Hinkins on the '' Hydrolysis of Triacetylglucose by Enzymes'' was not returned to the editor until after the time for publication of the November number of this JOURNAL, the following changes are to be made :

Page 370, line 34, for *guickly* read *quickly.*
" 371, " 14, " *emulsion, diastase, etc., can be* read *emulsin, and diastase, can be.*
Page 371, line 32, for *1 liter, and which was the $N/11.51$ acid* read *1 liter, which was $N/11.51$ acid.*
Page 372, line 27, place comma after *instance.*
" 375, " 36, " semicolon after *vary.*
" 380, last line, for $N/50$ read $N/40.$
" 384, line 14, for *0.85* read *0.83.*
" " " 26, insert *5.00* at the space ....
" " " 30, for $N/28$—*0.58* read $N/29$—*0.60.*
" 385 " 28, " *0.68* read *0.67.*
" " " 35, " $N/39$ " $N/39.50.$
" " " 38, " *7.90* read *7.00.*

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN COLORED SUBSTANCES DERIVED FROM NITRO COMPOUNDS.[1]

[FOURTH PAPER.]

BY C. LORING JACKSON AND R. B. EARLE.

The colored addition-compounds obtained from nitro de-
rivatives of benzol and sodic alcoholates, or other alkaline
bodies, have been the subject of frequent study. For an ac-
count of this work the reader is referred to the previous papers
from this laboratory.[2]

In these papers will be found convincing arguments against
Victor Meyer's theory that these compounds are formed by the
replacement by a metal of an atom of hydrogen attached to
the benzol ring. In a paper from the laboratory at Marburg,
published in 1899, Drost[3] describes some salts of the meta-
dinitroorthodinitrosobenzol, and gives analyses which seem
to indicate that they were formed by the replacement of 1
atom of hydrogen by 1 of the metals. As in this way he

[1] The work described in this paper formed part of a thesis presented to the
faculty of Arts and Sciences of Harvard University for the degree of Doctor of Science
by R. B. Earle.

[2] Jackson and Ittner: This JOURNAL, 19, 199; Jackson and Boos: *Ibid.*, 20, 444;
Jackson and Gazzolo: *Ibid.*, 23, 376.

[3] Ann. Chem. (Liebig), 307, 49.

revives the theory of Victor Meyer, it is necessary to discuss his work in detail. His salts were formed by the action of an alkaline carbonate or hydrate on the dinitrodinitrosobenzol ; if then they belong to the same class as the other salts from nitrobenzol derivatives, which seems probable from their properties, they should be formed by the addition of the metal and hydroxyl to the mother substance. This view of their composition was overlooked at first by Drost and Zincke,[1] as neither of them seemed to be aware of the work on this subject by Lobry de Bruyn,[2] and that from this laboratory,[3] which is not surprising, as it is almost impossible to look up the literature of a subject like this, which cannot be indexed under the names of definite compounds. In a later paper[4] Drost discusses these addition formulas, to which his attention was called by Hantzsch and Kissel's paper[5] (considered later), but rejects them on the ground of his analyses, especially that of the ammonium salt, and also because the compounds are formed from primary and secondary carbonates, which compels the assumption that the nitro compounds in aqueous solutions can behave as nitro acids, or that there is a hydrolytic decomposition of the carbonates. It seems to us that neither of these assumptions offers greater difficulties than the one made by Drost, that the hydrogen in the dinitrodinitrosobenzol is so loosely attached as to make it possible for this substance to decompose a carbonate in aqueous solution at 60° to 70°. Having disposed of this minor objection, the adoption of Drost's formulas rests on his analytical results, as should be the case. Accordingly, we compare below the percentages calculated by Drost for the salts, if formed by replacement of hydrogen with the metal, Drost's analytical results, and the percentages calculated if the salt was formed according to our view by the addition of metal and hydroxyl :

[1] Zincke and Schwartz : Ann. Chem. (Liebig), **307**, 32 (1899). Zincke's hypothesis of the formation of an unstable phenol, $C_6HNO_2(NO)_3OH$, in order to explain Drost's salts is unnecessary, if the salts prove to be addition- instead of substitution-compounds.

[2] Rec. trav. chim. Pays-Bas, **14**, 89.

[3] This JOURNAL, **19**, 203 ; **20**, 444 ; **23**, 376.

[4] Ann. Chem. (Liebig), **313**, 299 (1900).

[5] Ber. d. chem. Ges., **32**, 3137 (1899).

	Calculated for		
	$C_6HN_4O_6K + \frac{1}{2}H_2O.$	$C_6H_2N_4O_6OHK.$	Found.
	Drost's formula.	Our formula.	Drost.
C	26.34	25.52	26.33
K	14.32	13.87	14.13

	Calculated for		
	$C_6HN_4O_6Ag.$	$C_6H_2N_4O_6OHAg.$	Found.
Ag	32.40	30.77	30.65

	Calculated for		
	$C_6HN_4O_6NH_4.$	$C_6H_2N_4O_6OHNH_4.$	Found.
N	28.86	26.82	28.94

It appears from this comparison that the theory of Drost is supported by the nitrogen determination in the ammonium salt, but is not in harmony with the percentage of silver in the silver salt, and is only brought into close agreement with the percentages of potassium and carbon found by assuming that the potassium salt contains 0.5 molecule of water. The anhydrous salt would contain 27.26 per cent of carbon and 14.80 per cent of potassium. On the other hand, our theory is in agreement with the potassium, and silver might pass for the carbon, although it is not so good as Drost's, since it is below the percentage found, and does not agree with the nitrogen determination in the ammonium salt. The analytical results, therefore, are not incompatible with our formulas, especially when it is borne in mind that the silver salt, formed by precipitation, would probably be the purest of the salts analyzed, whereas the ammonium salt (which does not agree with our formula) had a brownish color, which may indicate decomposition. In the present condition of the subject we cannot accept Drost's analytical results as re-establishing Victor Meyer's theory that these salts are formed by the substitution of an atom of metal for an atom of hydrogen attached to the benzol ring. We hope that he will return to the subject and provide analytical material sufficient to decide finally between the two formulas, especially as he states that he does not consider his present data adequate.

The important paper of Hantzsch and Kissel,[1] although published before the paper by Gazzolo and one of us,[2] arrived

[1] Ber. d. chem. Ges., **32**, 3137.
[2] This JOURNAL, **23**, 376.

too late for proper discussion in it. They prepared the addition-compound from symmetrical trinitrotoluol and potassic methylate and succeeded in isolating from it the free acid, while all attempts to prepare the free acid from the corresponding benzol or xylol derivative failed.

By treating the free acid with acetyl chloride the acetyl derivative was obtained, which, as they point out, proves that these are true compounds instead of containing alcohol of crystallization according to Victor Meyer's theory. This point was also proved by determinations of molecular weight and electrical conductivity with some of these compounds.

In discussing the structure of these salts they pronounce in favor of the nitroester acid formula, I.,[1] but give no arguments

I.
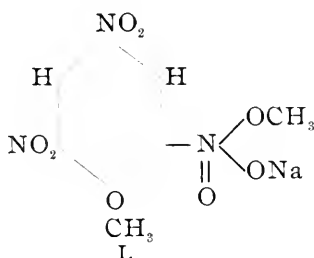
to prove its superiority to the quinoid formula, which apparently had not occurred to them as a possibility.[2]

In the paper by Gazzolo and one of us,[3] the formula I. and the quinoid formulas II. or III. were discussed and the preference given to the latter.

I. II.
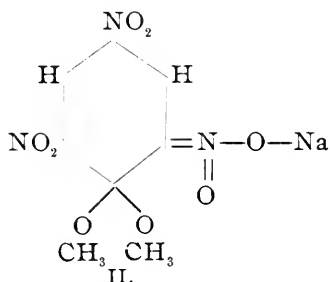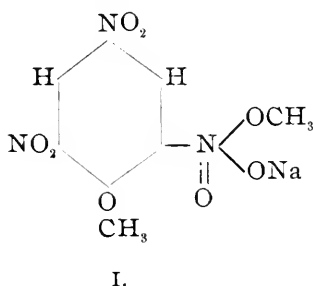
[1] All formulas in the discussion are those of the product from trinitroanisol and sodic methylate.

[2] Their paper led Angeli (Atti R. Accad. Lincei, [5], **9**, I., 41), to recall the fact that in 1897 (Gazz. chim. ital., **27**, II., 357) he was of the opinion that these substances were addition-compounds.

[3] This JOURNAL, **23**, 381.

$$O=N-ONa$$

III.
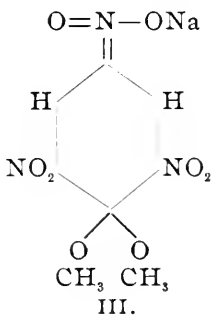
The arguments which led us to this conclusion will be given briefly as an introduction to the discussion based on more recent experimental data. Formula II. or III. is more in harmony with the following properties of the substance than formula I. is,—the strong color, the instability of the free acid, and the substitution of both methyl radicals by benzyl when the compound is allowed to stand with benzyl alcohol. For the full statement of these arguments the reader is referred to the paper[1] by Gazzolo and one of us, already cited.

Hantzsch and Kissel in their paper[2] furnish another strong argument in favor of formula II. or III., as they state that the free acid obtained by them, $C_6CH_3H_2(NO_2)_3HOCH_3$, is a weak acid, whereas, if it were a nitroester acid, it should be a very strong one, since Hantzsch and Rinckenberger[3] found that the analogous acid,

$$CH_3NO_2CH-NO\big<{OC_2H_5 \atop OH},$$
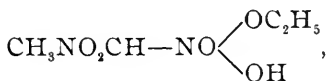
is ten times as strong as acetic acid. This fact they could not explain by formula I., but it at once becomes intelligible with formula II. or III., which puts the two acids in different classes. The strong color of the compounds also puzzled Hantzsch and Kissel, but is explained by the quinoid formulas.

[1] This JOURNAL, **23**, 381.

[2] Ber. d. chem. Ges., **32**, 3137.

[3] *Ibid.*, **32**, 628. In this paper the nitroester acid theory for these compounds is proposed.

The last paper[1] on this subject is one by Meisenheimer, which reached us while we were preparing this manuscript for the press.   He overlooked the paper by Jackson and Gazzolo[2] just cited, which is the more strange because he quotes the preceding paper[3] of this series.   This oversight has led him to publish as original the quinoid theory of these compounds, although a complete discussion of it had appeared in that paper two years earlier, including all the arguments from the properties of the bodies given by him.   To these he adds a proof of the quinoid theory similar to that given in this paper. This unnecessary duplication of work is certainly to be regretted.   In his experimental work he has failed to meet a serious objection to his proof, which it will be more convenient to discuss later in connection with the account of our own work.

The arguments from the properties of these bodies given above, while they create a strong presumption in favor of formula II. or III., do not constitute a final proof of this structure.   We accordingly tried to furnish a more convincing argument, and after spending much time in applying, without success, reactions to these substances which would show their affinity to quinones,[4] we at last hit upon an experiment which seems to us conclusive in favor of formula II. or III. This experiment consisted in preparing and analyzing an addition-compound containing two different alkyl radicals and studying the products of its decomposition with hydrochloric acid.   As it was necessary that the two radicals should be as different as possible, so as to make the analytical results decisive, we tried first the addition of sodic benzylate to trinitroanisol, but, as this proved unmanageable, we substituted sodic isoamylate for sodic benzylate, and with this obtained a compound, $C_6H_2(NO_2)_3OCH_3NaOC_5H_{11}$, the composition of which was established by three sodium determinations and a combustion.   It was necessary for our purpose to prove that this substance was a chemical individual, and the analyses did not
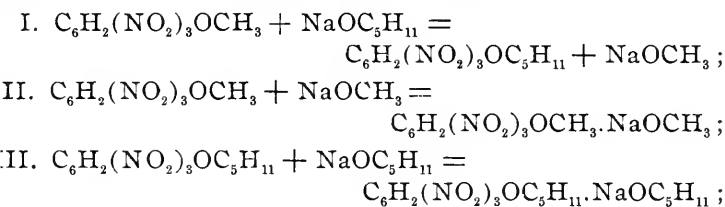
[1] Ann. Chem. (Liebig), **323**, 205.

[2] This JOURNAL, **23**, 376.

[3] Jackson and Boos : *Ibid.*, **20**, 444.

[4] A brief account of these experiments will be found in the experimental part of this paper.

lo this, since the following reactions might have taken place :

I. $C_6H_2(NO_2)_3OCH_3 + NaOC_5H_{11} =$
$$C_6H_2(NO_2)_3OC_5H_{11} + NaOCH_3 ;$$

II. $C_6H_2(NO_2)_3OCH_3 + NaOCH_3 =$
$$C_6H_2(NO_2)_3OCH_3 . NaOCH_3 ;$$

III. $C_6H_2(NO_2)_3OC_5H_{11} + NaOC_5H_{11} =$
$$C_6H_2(NO_2)_3OC_5H_{11} . NaOC_5H_{11} ;$$

which would give as the product a mixture in molecular pro-
portions of the dimethyl and the diisoamyl addition-com-
pounds. This mixture would give the same results on analy-
sis as the compound $C_6H_2(NO_2)_3OCH_3 . NaOC_5H_{11}$. The
chances that it was such a mixture were not very great, as the
product dissolved to a certain extent in the benzol used as a
precipitant in making it, and therefore we could have got our
concordant analytical results from a mixture only in case its
two components dissolved to exactly the same extent in ben-
zol, which was far from probable ; but as our proof of the
quinoid theory depended on the individuality of this product,
we felt it necessary to prove absolutely that it was a single
compound and not a mixture, and this we did by determining
its solubility and comparing it with those of its possible com-
ponents, for, although it is decomposed in time by water, it
can exist in an ice-cold solution for a long enough time to
carry out this determination. The solubilities found were as
follows :

100 parts of the solutions at $0°$ contain the following
amounts of the solids :

$C_6H_2(NO_2)_3OCH_3 . NaOC_5H_{11}$	1.508	1.110
$C_6H_2(NO_2)_3OCH_3 . NaOCH_3$	0.4751	0.6412
$C_6H_2(NO_2)_3OC_5H_{11} . NaOC_5H_{11}$	0.0960	0.0921

The conditions as to time occupied and mode of treatment
were as nearly identical as possible in all the determinations.
The want of close agreement in the results shows that the
solutions underwent some decomposition during the experi-
ments, but this is not sufficient to render them useless for our
purpose, as the difference between the lowest solubility of our
substance, $C_6H_2(NO_2)_3OCH_3 . NaOC_5H_{11}$, and the sum of the

highest determinations of its two components, if it were a mixture, is 0.3728, whereas the largest experimental error, that in the methylate compound, is 0.1661, so that there can be no doubt that our substance is a compound and not a mixture of constant composition.

The compound having been characterized in the way just given, it was next decomposed by treating a benzol solution of it with dilute hydrochloric acid. The product of this reaction began to melt at 62°, but did not become entirely liquid until 69°. From it we isolated isoamyl picrate, which was recognized by its melting-point, 68° to 69°, and by an analysis. That the other product of the reaction was trinitroanisol was proved by the fact that the presence of methoxyl was shown in it by the method of Zeisel, taken in connection with the melting-point of the crude product, 62° to 69° (trinitroanisol melts at 64°). This determination by the method of Zeisel also gave the amount of trinitroanisol present in the mixture. We found it to be 45.25 and 45.94 per cent. The percentage calculated, if the mixture consisted of trinitroanisol and isoamyl picrate in molecular proportions, is 44.83. The agreement is as near as could be expected. A rough method of determining the amount of isoamyl picrate was also tried, consisting in decomposing the mixture with potassic hydrate, extracting the amyl alcohol with chloroform, and weighing the dried amyl alcohol (which showed the proper boiling-point 131°); this gave 48 per cent of isoamyl picrate against 55.17 per cent calculated for a mixture in molecular proportions. The agreement is as close as could be expected considering the unavoidable losses entailed by the manipulations.

The result of the experiment, then, is that the compound $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$, when decomposed by hydrochloric acid, yields a mixture of trinitroanisol and isoamyl picrate in nearly molecular proportions. The formulas of the compound according to Hantzsch and Kissel's theory is given under IV., according to our theory under V. or VI.

$$\text{IV.}$$

NO₂ structure IV: with NO$_2$ (top), H, H, NO$_2$, —N(OC$_5$H$_{11}$)(ONa), O, O, CH$_3$.

$$\text{V.}$$

NO$_2$ (top), H, H, NO$_2$, =N—O—Na, ‖, O, O O, C$_5$H$_{11}$ CH$_3$.

$$\text{VI.}$$

O=N—ONa, ‖, H, H, NO$_2$, NO$_2$, O O, C$_5$H$_{11}$ CH$_3$.
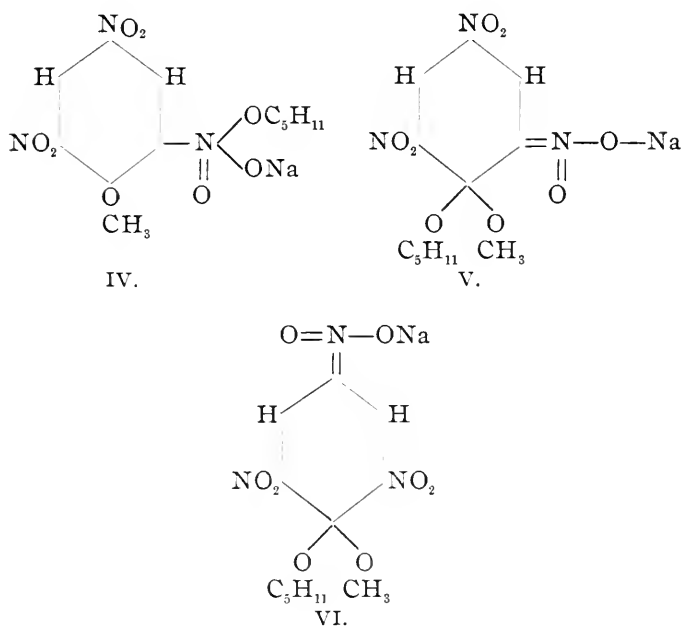
The explanation of the formation of isoamyl picrate from a substance with formula IV. necessitates a series of strained, improbable, molecular transformations, whereas the formation of equal molecules of trinitroanisol and isoamyl picrate by the decomposition of a body constituted as in formula V. or VI. is what would naturally occur by the splitting off of isoamyl alcohol from some molecules and methyl alcohol from others. This experiment, therefore, seems to give decisive evidence in favor of the quinoid theory.

It might be objected to the foregoing proof that perhaps the isoamyl picrate was not formed from the addition-compound, but was a result of the action of isoamyl alcohol on the trinitroanisol after it had been set free. This was met by an experiment which showed that isoamyl alcohol had no action on trinitroanisol.

As has been stated already, this proof was anticipated by Meisenheimer,[1] who studied the addition-products made from

[1] Ann. Chem. (Liebig), **323**, 242.

trinitroanisol and potassic ethylate, and from trinitrophenetol and potassic methylate. The composition of each substance was determined by complete analyses, and, after decomposition with sulphuric acid, ethyl picrate was isolated in each case. Similar results were obtained from the addition-compounds of trinitroanisol with potassic isobutylate, and isobutyl picrate with potassic methylate. The objection that these substances might be mixtures of

$$C_6H_2(NO_2)_3OCH_3.KOCH_3 \text{ and } C_6H_2(NO_2)_3OC_2H_5.KO.C_2H_5$$
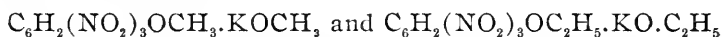
in molecular proportions was not met by Meisenheimer. Such a mixture might be formed by reactions similar to those given in the discussion of our work, or in another way peculiar to the experimental conditions used by Meisenheimer, since he made his addition-compound from trinitroanisol in ethyl alcohol solution, and it has been shown[1] repeatedly that one of these addition-compounds in contact with another alcohol is converted into the corresponding derivative of this alcohol. The ethyl alcohol therefore might well have formed enough of the ethyl compound to make the mixture. In fact it is strange that he obtained the methyl-ethyl rather than the di-ethyl compound. The explanation is probably to be found in the low temperature used by him.

The only marked difference between Meisenheimer's results and ours lies in the relative proportions of the two products. He thinks that more than 50 per cent of the picrate of the heavier alkyl radical is formed in every case, whereas our rough quantitative determinations pointed to a mixture of equal molecules. The cause of this discrepancy is probably to be found in the method of acidification or of purification of the product. Meisenheimer shook the salt with water and ether after acidifying with sulphuric acid. The ethereal solution of the decomposition-products was washed with sodic carbonate solution until it was almost colorless. The aqueous solution was colored dark reddish-brown. In our work the

---

[1] Jackson and Boos: This JOURNAL, **20**, 449; $C_6H_2(NO_2)_3OCH_3.NaOCH_3+2C_2H_5OH = C_6H_2(NO_2)_3OC_2H_5.NaOC_2H_5 + 2CH_3OH$; Jackson and Gazzolo: This JOURNAL, **23**, 394. Similar reactions with benzyl alcohol on the dimethyl compound, and methyl alcohol on the dibenzyl compound. These results are confirmed by the action of isoamyl alcohol on the dimethyl compound described later in this paper.

salt was suspended in benzol and shaken with dilute hydrochloric acid, the benzol solution washed with water, which showed no color, and the slightly yellow residue, after the benzol had been evaporated, washed with about 2 cc. of cold alcohol. The strong color in Meisenheimer's experiments certainly indicates a secondary reaction, perhaps autoxidation,[1] by which more trinitroanisol than trinitrophenetol may have been decomposed. On the other hand, the only chance for loss in our work lay in the washing with alcohol, but, as this removed only about 4 per cent of the total product (0.13 gram from 3 grams), it could not have had an appreciable influence on the proportions found by us. We feel constrained, therefore, to uphold our results against Meisenheimer's until the point is definitely settled by further experiments.

Meisenheimer suggests the name quinolnitro acids for these substances, which we adopt, as it seems to us better than the one we had invented. We have, however, in the experimental part of this paper named the salts after their components, adding the new names in parentheses, as we think this arrangement will be easier for the reader.

In our attempts to get characteristic quinone reactions from these bodies, the observation was made that when the addition-compound of trinitroanisol and sodic methylate (sodium salt of dinitrodimethoxyquinolnitro acid) was treated with aniline or hydroxylamine, both the methoxyl groups were driven out. This observation is in harmony with the quinoid theory, but, if the substance is a nitroester acid, there is no reason why more than one methoxyl should be displaced, since stable addition-products have been obtained from aromatic nitro bodies containing the anilido group. While this reaction yielded too indefinite aromatic products to be used as a proof of the quinoid theory, it seems to us to furnish a confirmatory argument in favor of it.

The only serious objection to the quinoid theory, which we have found, lies in the fact that the sodic malonic ester (or acetoacetic ester) compound derived from trinitroanisol is decomposed by acids with the utmost ease, with regeneration of

[1] Compare our study of the decomposition of the trinitrobenzoldimethylate described later in this paper.

trinitroanisol. If the sodic malonic ester splits into sodium and $-CH(COOC_2H_5)_2$ in order to make the addition, this, according to the quinoid theory, would give a union of the carbon of $-CH(COOC_2H_5)_2$ with the carbon of the benzol ring, which would be too stable to be broken up at once by dilute hydrochloric acid. The same difficulty, however, applies to Hantzsch and Kissel's nitroester theory, as in this case the carbon of the $-CH(COOC_2H_5)_2$ would form a stable union with the nitrogen of the nitro group, thus :

$$-N \underset{\substack{\| \\ O}}{\overset{\substack{O \\ \|}}{<}} \begin{matrix} O-Na \\ C(COOC_2H_5)_2 \\ H \end{matrix} .$$
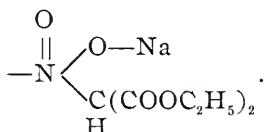
The difficulty can be removed in both cases by supposing the malonic ester residue is added in its tautomeric enol form; thus, $-O-C(OC_2H_5)=CH-COOC_2H_5$, when the less stable attachment of oxygen to carbon (or nitrogen) would be formed. This subject seems to us worthy of further study.

In considering the formation of both trinitroanisol and isoamyl picrate from the compound $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$ by acids it seemed probable to us that the relative amounts of the two products formed might depend on the amount of one or the other free alcohol present. In that case a decomposition carried on in the presence of an excess of methyl alcohol should consist principally in the removal of isoamyl alcohol, and should therefore give a larger proportion of the trinitroanisol than when the acidification took place only in benzol. An experiment showed, however, that a large excess of methyl alcohol had no effect whatever, no more trinitroanisol being formed in this case than when the decomposition took place in benzol alone.

It has been proved[1] that if the sodium salt of dinitrodimethoxyquinolnitro acid is boiled with ethyl alcohol the product, on decomposition with hydrochloric acid, yields ethyl picrate ; also that the same salt, if soaked in benzyl alcohol, yields with an acid benzyl picrate,[2] or, if the dibenzyl salt is

[1] Jackson and Boos ; This JOURNAL, **20**, 449.
[2] Jackson and Gazzolo : *Ibid.*, **23**, 394.

boiled with methyl alcohol, trinitroanisol is obtained on acidification ; but the only analysis of the salt of the new quinolnitro acid formed by the action of an alcohol was one of the diethyl compound formed by boiling the dimethyl body with ethyl alcohol, in which the difference in the percentages of sodium was too small to give conclusive results. It seemed of interest, therefore, to analyze a product where the difference in the size of the alkyl radicals would make the analytical results of some value. Accordingly, we treated the dimethyl compound with isoamyl alcohol at $70°$ for ten minutes, and found, by analysis of the product, that the following reaction had taken place :

$$C_6H_2(NO_2)_3OCH_3.NaOCH_3 + 2C_5H_{11}OH =$$
$$2CH_3OH + C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}.$$
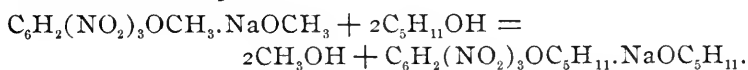
Delepine[1] has shown that an acetal boiled with a different alcohol and 1 to 3 drops of hydrochloric acid is in a short time converted into the acetal of the alcohol used. This reaction, therefore, is entirely in harmony with the quinoid acetal formula, but it seems hard to find a reason why the methoxyl attached to the ring (the anisol methoxyl) should be replaced by isoamyl alcohol, if the addition-compound is a nitroester acid, according to Hantzsch and Kissel, in view of the fact that trinitroanisol is entirely unaffected by isoamyl alcohol at $100°$. This argument for the quinoid theory was given in the paper by Gazzolo and one of us, but in a less exact form.

The experimental material at present collected is not sufficient to make it possible to decide whether these substances are ortho or paraquinoids. We hope that the work of the coming year in this laboratory will provide material for at least a partial solution of this problem.

The paper by Gazzolo and one of us contained descriptions of addition-compounds formed with sodic malonic ester, sodic acetoacetic ester, or sodic isoamylate, which contained 3 molecules of the alkaline substance to each molecule of the trinitro compound (trinitrobenzol or trinitroanisol), whereas all the addition-compounds previously analyzed contained only 1 molecule of the alkaline substance. In that paper addition-com-

[1] Compt. rend., **132**, 968.

pounds of sodic ethylate or methylate with trinitrobenzol were mentioned, which seemed to contain more than 1 molecule of alcoholate, but the formulas for which could not be established by the sodium determinations then alone at our disposal.   On returning to this subject, we soon found that the samples analyzed by Gazzolo had been decomposed, as the substance does not keep even *in vacuo*.   We accordingly prepared and dried samples of the methyl compound with as little delay as possible, and found it was formed by the addition of 2 molecules of sodic methylate to one of the trinitrobenzol, thus : $C_6H_3(NO_2)_3(NaOCH_3)_2$.   The spontaneous decomposition of this substance seems to consist in at least two parallel reactions.   In one, methyl groups are oxidized to formaldehyde by the oxygen of a nitro group, forming the tetranitroazoxybenzol, $(C_6H_3(NO_2)_2)_2N_2O$, melting at 183°, that was discovered by Lobry de Bruyn.[1]   The second reaction, which was made out with less certainty, seemed to consist in the formation of sodic nitrite and a nitrophenol.

This substance, $C_6H_3(NO_2)_3(CH_3ONa)_2$, is of interest, as it is the first which contains 2 molecules of an alcoholate.   It was formed even in the presence of a large excess (4 molecules) of the sodic methylate, and none of our attempts to prepare a methylate addition-compound containing more than 2 molecules of sodic methylate have been successful.   In our work we have succeeded in analyzing also the following addition-compounds containing 2 molecules of the alkaline material :

$$C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2 ;$$
$$C_6H_3(NO_2)_3(NaOC_6H_5)_2 ;$$
$$C_6H_2(NO_2)_3OCH_3(KCN)_2.$$
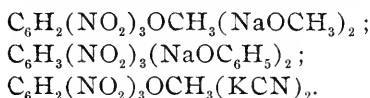
Of these, the first is the most interesting in this connection, because the mono compound, $C_6H_2(NO_2)_3OCH_3.NaOCH_3$,[2] is also known.   This compound, with 1 molecule of methylate, is a bright-red, crystalline substance of great stability for a substance of this class, remaining unaltered even when exposed to the air for a long time.   The compound

$$C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2,$$

[1] Rec. trav. chim. Pays-Bas, **13**, 151.
[2] This JOURNAL, **20**, 449.

on the other hand, is an orange, amorphous powder, which decomposes by spontaneous oxidation even *in vacuo*. That these dimolecular substances are compounds and not mixtures is shown by the fact that they were obtained of constant composition from solutions containing the factors in very different proportions. The formation of the dimethylate seems to depend on the conditions of the manufacture. If the product is precipitated with benzol, 2 molecules of the methylate are taken up. If, on the other hand, enough methyl alcohol is present to dissolve the substance so that the salt crystallizes out, there is a tendency to form the monomethylate body even in the presence of a large excess of sodic methylate. The same rule seems to apply to all cases as yet studied—precipitation gives products with more than 1 molecule of the alkaline constituent; crystallization gives those which contain but a single molecule.

The addition-product with sodic phenylate adds another alkaline material to those which give compounds of this class, for, although colored solutions had been obtained with this reagent, the product had not been analyzed heretofore. Hantzsch and Kissel[1] obtained from trinitrobenzol and potassic cyanide a compound containing only 1 molecule of potassic cyanide, $C_6H_3(NO_2)_3KCN$, and also prepared the corresponding acid. In our case 2 molecules were added, as already stated, $C_6H_2(NO_2)_3OCH_3(KCN)_2$. This was not unexpected, as the methyl alcohol solution was precipitated with benzol. The phenylate was precipitated with ether, which seems to produce the same effect as benzol.

In order to see whether a sulphonic group would promote the formation of these compounds in the same way that a carboxyl or third nitro group does, the symmetrical dinitrobenzolsulphonic acid was prepared, as described in a following paper, and from it we obtained the addition-product

$$[C_6H_3(NO_2)_2NaOCH_3SO_3]_2Ba.$$
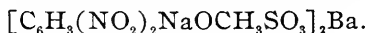
In looking up colored addition-compounds of this class in the literature, the difficulties already alluded to were encountered, so that we do not feel certain that our list is complete.

[1] Ber. d. chem. Ges., **32**, 3144.

In addition to those described by Drost,[1] of which we spoke at the beginning of this paper, Hantzsch and Kissel[2] have ob-tained a compound from paranitrobenzylnitramine,

$$C_6H_4NO_2CH_2N_2O_2Na.NaOC_2H_5,$$

and one formed by the action of baric hydrate on trinitroben-zoic acid in aqueous solution, which recalls the addition-com-pound of baric hydrate and trinitroanisol prepared by Boos and one of us.[3] Hillyer[4] also has obtained a carmine solution by the action of sodic methylate on dinitrophenoxozone, but he did not prepare the solid. The addition-compounds from amines and nitrobenzol derivatives probably belong to the same class as the salts of the quinolnitro acids, but the discus-sion of them does not fall within the scope of this paper.

EXPERIMENTAL PART.

Constitution of the Colored Substances. (*Quinolnitro Acids.*)

As has been explained in the introduction, the constitution of the colored addition-compounds was determined by the study of the product obtained from trinitroanisol and sodic isoamylate.

Preparation of Trinitroanisol.—The common process for making trinitroanisol from picryl chloride leaves much to be desired. Therefore, after some experiments, we have adopted the following method, which gives a good yield of trinitroani-sol with but little expenditure of time and labor, thus con-verting it into an easily accessible substance. Anisic acid was made from oil of anise by the method of Ladenburg and Fitz,[5] and 5 grams of this substance were added in small portions at a time to a mixture of 40 cc. of fuming nitric acid with the same volume of fuming sulphuric acid of sp. gr. 1.86. After all the anisic acid had been added, the mixture was warmed to 70° for two hours in a flask closed with a glass

[1] Ann. Chem. (Liebig), **307**, 49. In his paper (*Ibid.*, **313**, 299), Drost also de-scribes several color reactions from the corresponding toluol compounds, but gives no analyses of the salts.
[2] Ber. d. chem. Ges., **32**, 3137.
[3] This JOURNAL, **20**, 444.
[4] *Ibid.*, **26**, 361.
[5] Ann. Chem. (Liebig), **141**, 248 (1867).

bulb, care being taken that the temperature did not rise above 70°, as in that case a large amount of picric acid was formed. At the end of two hours the liquid was allowed to cool, then poured into ice-water, and purified by one crystallization from alcohol. The yield of crude anisic acid from the oil of anise is about 75 per cent of the theory, and from this anisic acid about 60 per cent of the theoretical yield of trinitroanisol is obtained.

Addition-Compound of Trinitroanisol and Sodic Isoamylate. (*Sodium Salt of Dinitromethoxyisoamyloxyquinolnitro Acid.*)— To a solution of 2 grams of trinitroanisol in anhydrous benzol a solution of sodic isoamylate was added, prepared by the action of isoamyl alcohol in excess on 0.09 gram of sodium. The amount of trinitroanisol, therefore, was more than twice that needed, if it were mixed with the sodic isoamylate in the proportion of equal molecules. This large excess seemed to be necessary to prevent the formation of addition-compounds containing more than 1 molecule of the isoamylate. For the same reason the mixture was frequently stirred, while it stood for half an hour at ordinary temperatures, to complete the reaction. The bright-red, amorphous precipitate thus obtained was filtered out, washed thoroughly with dry benzol, and after being dried, at first on a porous plate and afterward *in vacuo*, it was analyzed with the following results :

    I. 0.3262 gram substance gave 0.0683 gram Na_2SO_4.

    II. 0.5073 gram substance gave 0.1116 gram Na_2SO_4.

    III. 0.5320 gram substance gave 0.1140 gram Na_2SO_4.

    IV. 0.2060 gram substance gave, on combustion, 0.3056 gram CO_2 and 0.0908 gram H_2O. In order to decompose the salt, the substance was mixed with a large excess of a mixture of 8 parts of fused plumbic chromate with one of potassic dichromate, and to lessen the chances of explosion this was spread out in four long porcelain boats.

	Calculated for $C_6H_2(NO_2)_3OCH_3(NaOC_5H_{11})$.	I.	II.	III.	IV.
Na	6.52	6.79	7.13	6.95	....
C	40.80	....	....	....	40.46
H	4.53	....	....	....	4.90

The substance is a bright crimson powder, usually amorphous, but in one experiment it was obtained in short, microscopic prisms. It is decidedly stable for one of these bodies, as it can be kept *in vacuo* for an indefinite time without apparent decomposition, and, even when exposed to the air, it does not deliquesce or change its appearance to a marked extent inside of eight hours. It dissolves in ice-water with a deep-red color, and the solution, if kept at o°, remains clear for about fifteen minutes. At the end of this time a turbidity begins to appear, and this decomposition continues to take place slowly afterward. Dilute acids decompose it instantly.

As the analyses given above were made with samples from different preparations, there could be no doubt that the substance had a constant composition, but it was possible that it was not a single compound, since it might be a mixture in molecular proportions of $C_6H_2(NO_2)_3OCH_3.NaOCH_3$ and $C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$, which, on analysis, would give such results as we obtained. As our proof of the constitution of this body depended on its individuality, it was necessary for us to remove the doubt suggested above, and we did this by comparing the solubility of our substance with those of its two components, if it were a mixture. Fortunately, the solutions of these bodies in ice-water were stable for a sufficiently long time to admit of determinations near enough for our purpose. The solubilities were tried by the method of Victor Meyer. The substance was stirred with water at o° for ten minutes, then filtered, and the amount of matter dissolved determined by evaporating with sulphuric acid and weighing the sodic sulphate formed.

Solubility of $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$:

I. 28.69 grams solution, at o°, yielded 0.0870 gram Na_2SO_4.

II. 50.16 grams solution yielded 0.1113 gram Na_2SO_4.

100 parts of the solution, at o°, contain the following number of parts:

	I.	II.
$C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$	1.508	1.110

Solubility of $C_6H_2(NO_2)_3OCH_3.NaOCH_3$:

III. 45.08 grams solution, at o°, yielded 0.0512 gram Na_2SO_4.

IV. 33.92 grams solution yielded 0.0520 gram Na_2SO_4.

100 parts of the solution, at 0°, contain the following number of parts :

	III.	IV.
$C_6H_2(NO_2)_3OCH_3.NaOCH_3$	0.4751	0.6412

Solubility of $C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$:

V. 34.20 grams solution, at 0°, yielded 0.0057 gram Na_2SO_4.
VI. 30.02 grams solution yielded 0.0048 gram Na_2SO_4.

100 parts of the solution, at 0°, contain the following number of parts :

	V.	VI.
$C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$	0.0960	0.0921

These results show wide variations, obviously due to varying amounts of decomposition in the solutions, although the length of time and mode of treatment were kept as nearly uniform as possible in all the determinations. In spite of these experimental errors, however, the results prove that our substance was not a mixture of these two compounds, since the sum of the two highest determinations of the solubility of the components (IV., 0.6412 ; V., 0.0960) was 0.7372, the lowest solubility for our substance was (II.) 1.1100, which is 0.3728 higher than the solubility corresponding to a mixture, whereas the worst experimental error (between III. and IV.) is 0.1661, less than half of this. A confirmatory argument will be found in the introduction.

The Products of the Decomposition of the Addition-Product from Trinitroanisol and Sodic Isoamylate, $C_6H_2(NO_2)_3OCH_3$. $NaOC_5H_{11}$.—After a preliminary experiment had shown us that one of the products of decomposition gave off a strong odor of isoamyl alcohol, when boiled with potassic hydrate, we proceeded as follows : Ten grams of the addition-compound were suspended in benzol and shaken with dilute hydrochloric acid (1 : 10). The color disappeared and the solid matter went into solution. The layer of benzol was then washed with water and the benzol evaporated off on the steam-bath. The residue solidified, on standing, to a gummy mass which was washed with about 2 cc. of cold alcohol to remove

the liquid (principally amyl alcohol) that had not dissolved in the water. The amount of alcohol used was kept as small as possible, so as to reduce to a minimum any solution of the solid products, and the quantity of substance removed by this washing was only 0.13 gram from 3 grams of the decomposition-products. The product was then treated with hot ligroin, as we had found that while isoamyl picrate is freely soluble in this solvent, trinitroanisol is comparatively insoluble in it. After the ligroin had dissolved nearly half of the product it was evaporated to dryness, and the crystals thus obtained again extracted with hot ligroin, rejecting the insoluble portion as before. The extract was then recrystallized from hot ligroin until it showed a constant melting-point, which proved to be 68° to 69°, the melting-point of isoamyl picrate. For greater certainty it was dried *in vacuo* and analyzed with the following result :

0.1980 gram substance gave, on combustion, 0.3246 gram CO_2 and 0.0880 gram H_2O.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}$.	Found.
C	44.14	44.70
H	4.34	4.94

This proves that isoamyl picrate is one of the products of the decomposition with acids of the addition-compound of trinitroanisol and sodic isoamylate. That another product is trinitroanisol was made probable by the fact that the crude decomposition-product melted from 62° to 69° (trinitroanisol melts at 64°, the isoamyl picrate at 68° to 69°) and was proved by a determination of the presence of the methoxyl radical in this crude product, which, as it was made quantitatively, also threw light on the relative amounts of the two principal decomposition-products.

I. 0.4091 gram decomposition-products washed with a little alcohol and dried on a porous plate and *in vacuo* gave, by the method of Zeisel,[1] 0.1787 gram argentic iodide.

II. 0.3973 gram substance gave 0.1762 gram argentic iodide.

[1] Monatsh. Chem., **6**, 989; **7**, 406; or Sitzber. Akad. Wiss. Wien., **92**, [2], 1431 ; **94**, [2], 341.

	I.	II.
Trinitroanisol	45.25	45.94

If the mixture was composed of equal molecules of trinitroanisol and isoamyl picrate, the percentage of trinitroanisol would be 44.83. It would seem probable, therefore, that the two products were formed in equal amounts. In order to get an approximate determination of the quantity of isoamyl picrate formed, 6.7 grams of the decomposition-product, prepared as above, were boiled for two hours with 60 cc. of a solution of potassic hydrate (1 : 10) in a flask with a return-condenser. After the liquid had cooled it was extracted four times with chloroform, the chloroform solution washed thoroughly with water, and dried over fused potassic disulphate. The chloroform was then distilled off carefully and the residue heated until the traces of water, which had escaped the drying agent, had also passed over, keeping the temperature well below the boiling-point of isoamyl alcohol. The residue weighed 0.947 gram, and, after weighing, its boiling-point was found to be 131°, showing that it was isoamyl alcohol. The percentage of isoamyl picrate calculated from this weight of isoamyl alcohol is 48 instead of 55.17 required, if the mixture is composed of equal molecules of the two substances. The agreement is as close as can be expected when the unavoidable losses in the method used are considered.

To meet the objection that the isoamyl picrate in the decomposition-product might have been formed by the action of isoamyl alcohol on the trinitroanisol, after the decomposition with acid had taken place, 0.5 gram of trinitroanisol was heated with a little isoamyl alcohol on the steam-bath for half an hour. After the mixture had cooled, the isoamyl alcohol was removed by washing with a little alcohol and the residue dried on a porous plate and *in vacuo*.

0.2263 gram substance gave, by the method of Zeisel, 0.2126 gram of argentic iodide.

	Per cent.
Trinitroanisol	97.07

This result shows that the action of isoamyl alcohol on trinitroanisol was insignificant in amount, if it acted at all. It is

probable that there is no action whatever, since the difference of 2.93 per cent between the trinitroanisol recovered and that taken is not larger than would be expected from adhering iso-amyl alcohol, which could not be wholly removed by the single washing with a little cold alcohol. Thorough washing or crystallization was inadmissible as it might have removed the product of the reaction.

After we had shown that the addition-compound from trinitro-anisol and sodic isoamylate gave, on acidification, equal mole-cules of trinitroanisol and isoamyl picrate, it became of inter-est to study the effect of the presence of an alcohol, since it seemed probable that this might have an influence on the pro-portions formed. An experiment was tried, accordingly, in which a considerable amount of methyl alcohol was added to the benzol solution before acidification. The determination of the methoxyl in the product is the one numbered II., al-ready given, and gave essentially the same amount as I., in which no methyl alcohol was used. It seems, therefore, that the presence of the methyl alcohol has no effect on the rela-tive amounts of the products of the decomposition of this mixed addition-compound.

Conversion of the Addition-Compound of Trinitroanisol and Sodic Methylate into the Isoamyl Compound.—The work of Gaz-zolo and one of us[1] has shown that benzyl picrate is formed by the acidification of the product of the action of benzyl alcohol on the addition-compound of trinitroanisol and sodic methyl-ate, and that trinitroanisol is formed by acidification after methyl alcohol has acted on the dibenzyl addition-compound, but in neither case was the intermediate addition-compound formed by the action of the alcohol analyzed. Boos and one of us[2] analyzed the ethyl-ethylate compound,

$$C_6H_2(NO_2)_3OC_2H_5NaOC_2H_5,$$

formed by the action of ethyl alcohol on

$$C_6H_2(NO_2)_3OCH_3.NaOCH_3,$$

but the percentages of sodium in these compounds are so near

[1] This JOURNAL, **23**, 394.
[2] *Ibid.,* **20**, 449.

each other that the analysis was not of much value, the proof that it was the ethyl compound being furnished in this case (as in the work of Gazzolo) by the isolation of the ethyl picrate. It seemed desirable, therefore, to try the conversion of one addition-compound into another by means of an alcohol, testing the composition of the addition-product formed by analysis. We chose for this work the methyl compound treated with isoamyl alcohol, as the difference between the radicals was sufficiently great to give unmistakable results on analysis. One gram of $C_6H_2(NO_2)_3OCH_3.NaOCH_3$ was mixed with 10 cc. of isoamyl alcohol and the mixture warmed to $70°$ for about ten minutes, when it was found that the solid had disappeared, giving a deep-red solution. After the liquid had cooled it was poured into a large excess of benzol and the red precipitate washed first with benzol, and afterward many times with cold water. It was then dried at $100°$ and analyzed with the following result :

0.5070 gram substance gave 0.0948 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$.	Found.
Na	5.62	6.06

$C_6H_2(NO_2)_3OCH_3.NaOCH_3$ would give 7.69 per cent of sodium. There can be no doubt from this result that the isoamylate addition-compound is formed under these conditions.

Other Experiments on the Constitution of the Addition-Compounds. (*Quinolnitro Acids.*)—In this section we give some account of our attempts to determine the structure of these colored bodies, before we took up the method already described, which led to the desired result. As these experiments were not fully successful, we describe them only briefly.

The action of aniline on $C_6H_2(NO_2)_3OCH_3.NaOCH_3$ was tried in the hope that it would replace the two methoxyl groups with the formation of an anil,

$$C_6H_2(NO_2)_2(NO_2Na)=NC_6H_5.$$

Upon carrying out the decomposition in a flask, and distilling over the methyl alcohol set free into a Zeisel apparatus, it was found that both the methoxyl groups were driven out (found

19.23 and 19.05 per cent of methoxyl instead of 20.87 per cent calculated for $2CH_3O$). The other product of the reaction was a red salt which we did not succeed in purifying[1] even when all the work was carried on in an atmosphere of hydrogen. Upon acidification picrylanilid, $C_6H_2(NO_2)_3NHC_6H_5$, was obtained, which was recognized by its melting-point, $175°$, so that the red sodium salt was evidently the picrylanilid salt, $C_6H_2(NO_2)_3NNaC_6H_5$. We also found that there was the strongest similarity between our specimen and one made directly from the anilid. This result can be explained on the quinoid theory by supposing that the first product of the reaction (I.) changed spontaneously into the anilid salt (II.), an
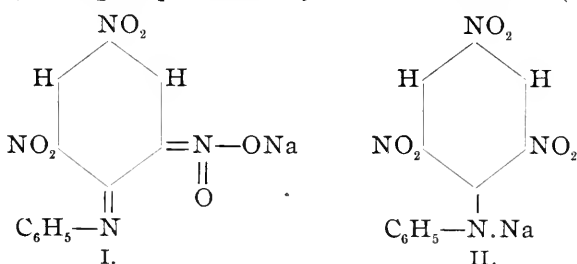
explanation, which seems very probable, whereas, if Hantzsch and Kissel's nitroester acid theory is adopted, it is hard to see why the methoxyl attached to the nitro group should be driven out by aniline, especially since picramide forms an addition-compound with sodic methylate, and it is therefore probable that the corresponding picrylanilid compound would be stable enough to exist. It is obvious, however, that no proof of the structure of the addition-compound can be based on such indefinite results.

Hydroxylamine in alcoholic solution gave a result exactly similar to that just described in the case of aniline, the sodium salt of picrylhydroxylamine, and 2 molecules of methyl alcohol being formed. Phenylhydrazine acted on the substance with too great violence to give good results. At $100°$ the mixture took fire in a few minutes, and even in the cold the action was so energetic that black, tarry products were formed.

---

[1] The amount of sodium in two different samples differed by 1 per cent, and both were much higher than that calculated from the formula.

In the hope that replacement of the sodium by an organic radical would form a more stable product, which might give conclusive results with aniline or hydroxylamine, some time was spent in trying the action on

$$C_6H_2(NO_2)_3OCH_3.NaOCH_3$$

of dimethyl sulphate,[1] methyl iodide, acetyl chloride, or benzoyl chloride, but in no case was any result obtained. These experiments confirm the negative results previously obtained by Gazzolo and one of us,[2] and convince us that further experiments in this line are not worth while. Hantzsch and Kissel[3] obtained their acetyl derivative from the free acid.

Experiments were also tried with oxidizing agents on some of the addition-compounds of trinitrobenzol in the hope of removing an atom of hydrogen and the sodium, and thus arriving at a substituted trinitrobenzol. Potassic permanganate gave some not unpromising results, but the work was not continued, because we had proved the constitution of the substances in another way.

Nearly related to these was the attempt to convert Hantzsch and Kissel's addition-product from trinitrobenzol and potassic cyanide,[4] $C_6H_3(NO_2)_3KCN$, into picryl cyanide by the action of bromine. The products of the reaction were black tars, from which we could not isolate any definite substance. A few experiments on the preparation of the as yet undescribed picryl cyanide showed that it is not an easy substance to make.

Experiments along the line which finally led to successful results, consisted in trying to isolate an addition-product of picryl chloride and sodic methylate, which, if it exists, is too unstable for study ; and work upon the mixed addition-compound from trinitroanisol and acetoacetic ester. If picrylacetoacetic ester could be detected in the products of the decomposition of this body, when an acid is added to it, it would be a strong argument for the quinoid formula. Unfor-

[1] Claesson and Lundvall : Ber. d. chem. Ges., **13**, 1699.

[2] This JOURNAL, **23**, 395.

[3] Ber. d. chem. Ges., **32**, 3141 (1899).

[4] *Ibid.*, **32**, 3144 (1899).

tunately, we could obtain by the acidification of this substance only unmanageable tars, from which nothing definite could be isolated.   By using phenyl picrate or parabromortho-nitrophenyl picrate in place of trinitroanisol, the picrylaceto-acetic ester,[1] melting at 97° to 98°, was obtained, and the formation of this ester seemed to be preceded by that of colored compounds, but, as these compounds were too unstable to be collected, purified, and dried for analysis, so as to show that they contained both the phenyl and acetoacetic ester radicals, these experiments were of little value for our purpose.

Addition-Compound from Trinitrobenzol and Sodic Methylate. (*Sodium Salt of Nitrodimethoxydiquinolnitro Acid.*)—Gazzolo and one of us[2] obtained, by the action of sodic methylate (or ethylate) on trinitrobenzol and precipitation of the salt thus formed with benzol, red substances of slight stability, which gave percentages of sodium corresponding to the formula

$$C_6H_3(NO_2)_3(NaOCH_3)_3CH_3OH$$

(or the ethyl compound).   As stated in that paper, more analytical data were necessary before any formula could be considered established for these substances, and, accordingly, we took up the study of this subject.   When we tried to make the methyl derivative as before with 3 molecules of sodic methylate to one of trinitrobenzol, we got different results from different preparations, varying from 13.10 to 15.02 per cent of sodium, and it was not until we had increased the proportion of sodic methylate to 4 molecules that we got a result of 17 per cent of sodium, corresponding to the 16.94 per cent required by the formula given above.   If, on the other hand, the amount of sodic methylate was reduced to 1 molecule, the sodium determinations in the salt came out between the percentages required for the addition of 1 and 2 molecules of sodic methylate.   It was evident from these preliminary experiments that the substance was not fit for analysis, either because no constant product was formed or because it suffered decomposition during the preparation for analysis.

[1] Dittrich : Ber. d. chem. Ges., **23**, 2720 (1890).
[2] This JOURNAL, **23**, 391.

Determinations, by the method of Zeisel, of the number of methoxyl groups contained in the substance, gave results showing that there was only one methoxyl group in it instead of the four required by the formula provisionally assigned to it. Further, as this amount was too small to correspond to the percentage of sodium found, we were led to the conclusion that the substance had undergone decomposition between its preparation and analysis. We accordingly prepared two fresh samples, and dried the precipitates formed by the benzol at 60° in a stream of dry hydrogen for half an hour, all the other operations being also carried on as quickly as possible. The analyses gave the following results :

I. 0.3223 gram substance gave 0.1455 gram Na_2SO_4.

II. 0.3100 gram substance gave 0.1426 gram Na_2SO_4.

	Calculated for $C_6H_3(NO_2)_3(CH_2ONa)_2$.	I.	Found. II.
Na	14.33	14.62	14.90

There can be no doubt that the substance is formed from the trinitrobenzol by the addition of 2 molecules of sodic methylate.

It is a red, amorphous substance, which decomposes in a few hours, even *in vacuo*. Exposed to the air it deliquesces and becomes tarry in a very short time. If it is heated suddenly to 100° it explodes with great violence, but if the temperature is raised gradually it can be heated to 150° with no apparent change except a slight darkening of the color. Even at this temperature no alcohol is given off.

Decomposition of the Addition-Compound from Trinitrobenzol and Two Molecules of Sodic Methylate.—As stated in the preceding section, this addition-compound decomposes rapidly, even when kept in a vacuum desiccator. In taking up the study of this decomposition we first established the facts that the compound, when acidified immediately after preparation, gave unaltered trinitrobenzol, but after standing three days *in vacuo* no trinitrobenzol was obtained on acidification. Instead of this an amorphous, clay-colored mass was formed, weighing about half as much as the expected trinitrobenzol, while the filtrate had a deep-red color, smelt strongly of formalde-

hyde, and reduced Fehling's solution, or ammoniacal argentic nitrate. In order to obtain a better separation of the products, a second sample, prepared in the same way, was treated with water, filtered, and the filtrate acidified with dilute hydrochloric acid. The residue insoluble in water was recrystallized from strong nitric acid until it showed a constant melting-point, and as this lay at 183° it was evidently the tetranitroazoxybenzol,

$$C_6H_2(NO_2)_2—N \overset{\displaystyle O}{\diagdown\diagup} N—C_6H_2(NO_2)_2,$$
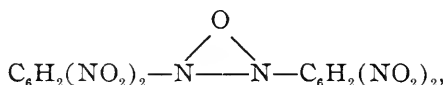
discovered by Lobry de Bruyn.[1] The aqueous filtrate gave a strong test for a nitrite. The precipitate formed by the hydrochloric acid was a sticky substance, the nature of which we have not succeeded in determining, but we think it probably contained picric acid, or some similar nitrophenol, as it gave a deep-brown color with an aqueous solution of potassic cyanide, and formed red salts with solutions of the alkalies. The filtrate from this hydrochloric acid precipitate contained apparently a variety of substances, but they were so unmanageable that we did not succeed in recognizing any of them but formaldehyde, which was detected by the properties already mentioned. That the formaldehyde was a principal product of the reaction was shown by a quantitative determination according to Orchard.[2] This gave about quarter the amount which would have been formed if all the methoxyl groups had been oxidized to it. It should be remembered, in this connection, that the specimen had stood *in vacuo* for three days.

An experiment was also tried to determine whether the decomposition, when carried on in air, was attended with a gain or loss in weight, and it was found that the weight of a sample became constant after standing for two months in a desiccator over calcic chloride, and that there had been a loss in weight amounting to 12.66 per cent.

From these observations it seems evident that two or more

[1] Rec. trav. chim. Pays-Bas, **13,** 151.
[2] Chem. Centrbl., 1897, 1, 441 ; Analyst, **22,** 4.

reactions take place during the decomposition of the addition-compound of trinitrobenzol and 2 molecules of sodic methylate. One of these consists essentially in the oxidation of one or more of the methoxyl groups to formaldehyde by the oxygen of two nitro groups which form the tetranitroazoxybenzol, and, as this reaction takes place independently of the surrounding atmosphere, it accounts for the slight stability of the substance. A second reaction was indicated by the formation of nitrite and probably of some nitrophenol.

Addition-Compound from Trinitroanisol with Two Molecules of Sodic Methylate, $C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2$.—To a solution of trinitroanisol in anhydrous benzol was added a methyl alcohol solution of sodic methylate in large excess, 3 to 4 molecules of sodic methylate to each molecule of the trinitroanisol. The precipitate appeared in yellow, gummy masses, which were thoroughly washed with benzol, when they became hard and granular. They were dried on a porous plate and then *in vacuo* at 60° for half an hour, and were analyzed immediately with the following result:

    I. 0.3672 gram substance gave 0.1526 gram Na_2SO_4.
    II. 0.3392 gram substance gave 0.1310 gram Na_2SO_4.
    III. 0.3218 gram substance gave 0.1262 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2$.	I.	Found. II.	III.
Na	13.13	13.48	12.52	12.72

As the three analyses were made with three different preparations, there can be no doubt that the substance is a definite compound.

Properties of the Sodium Salt of Nitrotrimethoxydiquinolnitro Acid, $C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2$.—It is an amorphous, orange-colored powder, and is much less stable than the corresponding compound containing 1 molecule of methylate, for, although it changes little in appearance on standing *in vacuo*, analyses show that it has undergone a decomposition similar to that just described in the case of the trinitrobenzoldimethylate compound. It is freely soluble in water. It shows no change in appearance, even when heated as high as 150°, but from what has just been said of its behavior *in vacuo*, it is

evident that this observation does not prove that it remains unaltered at this temperature.

Addition-Compound of Trinitroanisol and Potassic Cyanide (*Potassium Salt of Nitrodicyandiquinolnitro Acid*), $C_6H_2(NO_2)_3OCH_3(KCN)_2$.—A solution of 1.2 grams of trinitroanisol in 20 cc. of methyl alcohol was mixed with 0.5 gram of finely powdered potassic cyanide (that is, somewhat less than 2 molecules of cyanide to each molecule of trinitroanisol), and the mixture shaken for five minutes. It was filtered quickly with the pump and the filtrate diluted with 100 cc. of anhydrous benzol. After standing for a few minutes the precipitate thus obtained was filtered out, washed with benzol, and dried on a porous plate and *in vacuo*, after which it was analyzed with the following result :

I. 0.2491 gram substance gave 0.1176 gram K_2SO_4.

II. 0.2284 gram substance gave 0.1058 gram K_2SO_4.

	Calculated for $C_6H_2(NO_2)_3OCH_3(KCN)_2$.	Found. I.	II.
K	20.95	21.19	20.82

The analyses were made with different preparations.

The addition-compound is a dark, reddish-brown, amorphous substance, freely soluble in water or alcohol, and decidedly unstable.

Addition-Compound of Trinitrobenzol and Sodic Phenylate (*Sodium Salt of Nitrodiphenoxydiquinolnitro Acid*), $C_6H_3(NO_2)_3(NaOC_6H_5)_2$.—To a solution of 0.5 gram of trinitrobenzol in a mixture of absolute ether and phenol was added the sodic phenylate obtained by treating 0.22 gram of sodium with phenol mixed with a little ether, that is, about twice the theoretical amount of sodic phenylate was used. The mixture was allowed to stand about fifteen minutes with frequent stirring, after which the precipitate was filtered out and washed, at first with absolute ether containing a little phenol, since we found this would dissolve sodic phenylate, and finally with pure ether. The substance was dried on a porous plate and *in vacuo*, and analyzed as soon as possible, with the following results :

I. 0.2086 gram substance gave 0.0653 gram Na_2SO_4.

II. 0.2231 gram substance gave 0.0665 gram Na_2SO_4.

	Calculated for $C_6H_3(NO_2)_3(NaOC_6H_5)_2$.	Found. I.	II.
Na	10.34	10.15	9.67

The analyses were made with different preparations.

The substance is a bright, brick-red, amorphous powder, and is decomposed immediately by the addition of water. It is, in fact, one of the least stable of these compounds which have been analyzed.

Addition-Compound of Baric Dinitrobenzolsulphonate and Sodic Methylate (Barium Sodium Salt of Nitrosulphomethoxy-quinolnitro Acid), $[C_6H_3(NO_2)_2NaOCH_3SO_3]_2Ba$.—The sodic methylate, prepared by adding 0.1 gram of sodium to some methyl alcohol mixed with a large excess of anhydrous benzol, was mixed with a solution in methyl alcohol of 0.5 gram of the baric dinitrobenzolsulphonate, $SO_3I(NO_2)_23.5$, prepared as described in a subsequent paper. This gives 4 molecules of the methylate to each molecule of the salt. The solution turned deep-red, but nothing separated even after standing a short time; an excess of benzol was therefore added, which precipitated a dark-red, amorphous mass. This precipitate was filtered out, washed thoroughly with benzol, and then dried on a porous plate and *in vacuo* at 60°. The analysis gave the following results :

I. 0.2072 gram substance gave 0.1070 gram of the mixture of baric and sodic sulphates.

II. 0.2302 gram substance gave 0.1178 gram of the mixture of baric and sodic sulphates.

	Calculated for $[C_6H_3(NO_2)_3NaOCH_3SO_3]_2Ba$.	Found. I.	II.
Ba + Na	24.77	25.21	24.98

The substance is an amorphous, pale salmon-colored powder when dry, but takes on a deep-red color when moistened with benzol, chloroform, or ligroin. This change of color is very striking. It is soluble in water or in methyl or ethyl alcohol, but insoluble in all the other common solvents. It is apparently one of the more stable compounds of this class, as

it undergoes no change in appearance, even when exposed to the air for a long time.

Some attempts to obtain a colored addition-compound from Willgerodt's[1] picrylsulphonic acid led to no definite results, for, although a colored substance was obtained on adding sodic methylate to the free acid, we did not feel certain that this was a derivative of the picrylsulphonic acid, since this substance is decomposed with great ease by alkaline solutions. This color, therefore, might be due to a trinitroanisol derivative, and under these circumstances we did not feel that the subject was of enough importance to spend time in making analyses.

Sodic acetoacetic ester gave a deep-red coloration with phenyl picrate, but we made no attempt to isolate the substance (which may not belong to this class), contenting ourselves with the study of its decomposition-product, which will be described in a later paper.

XXXVIII.—THE DECOMPOSITION OF DIAZONIUM SALTS WITH PHENOLS.

By James F. Norris, B. G. Macintire, and W. M. Corse.

Some time ago Hirsch[2] undertook a careful study of the preparation of phenol from aniline by means of the diazo reaction, on account of the fact that the yield of phenol was much less than that required theoretically by the equation usually written to express the decomposition of a diazonium salt with water. It was found that a number of reactions take place simultaneously. Among the products of the decomposition was p-oxydiphenyl. This compound was shown to be the product of the action of the diazonium salt on a part of the phenol produced in the decomposition. As a result of the study of this reaction, Hirsch showed that when a cold aqueous solution of a diazonium salt was treated with a large

[1] J. prakt. Chem., [2], **32**, 117 (1885).
[2] Ber. d. chem. Ges., **23**, 3705 ; **25**, 1973.

quantity of phenol, the diazo compound was extracted from the water. The phenol solution was stable in the cold, but decomposed when heated, with the evolution of nitrogen and the formation of oxydiphenyl, phenyl ether, and ill-defined products which were not isolated. Hirsch endeavored, without success, to extract diazonium salts from an aqueous solution by substances other than phenol. This method of preparing diphenyl derivatives was, therefore, limited to the decomposition of various diazo compounds with this one substance. The method was not a very satisfactory one in that large quantities of phenol were used in the extractions, and a number of fractional distillations were involved.

In studying the preparation of phenol from aniline, in this laboratory, we were led to the view that when a diazonium salt decomposes in the presence of water and a phenol, it reacts to a much larger extent with the phenol than with the water. It seemed possible, therefore, that the preparation of diphenyl derivatives by this reaction might be carried out in aqueous solution, and that the method might be developed into a general one for the preparation of hydroxyl derivatives of diphenyl by using, instead of phenol, other compounds of the same class. To test this view, experiments were carried out with benzenediazonium salts and phenol, pyrocatechin, resorcin, and hydroquinone. It was found that the phenols entered into the reaction when the decomposition of the diazonium compound took place at 75° to 100°, and that good yields of diphenyl derivatives were obtained.

In carrying out the reaction, the phenol, mixed with a small quantity of water and heated to about 90°, was treated cautiously with a cold aqueous solution of the diazonium salt. A vigorous reaction took place, nitrogen was evolved, and a dark, heavy oil separated. When phenol was used, the reaction-product was found to consist of *p*-oxydiphenyl, *o*-oxydiphenyl, phenyl ether, and a tarry mass which could not be purified in any way. The amount of oxydiphenyl obtained was equal to about one-half the weight of aniline used. The reaction furnishes, therefore, a good method for the preparation of this compound. The diphenyl compounds were sepa-

rated from the reaction-mixture by distillation with super-heated steam. This method appears to be much more expeditious than fractional distillation, which has been used in the past.

The experiments show that by means of benzenediazonium salts a phenyl group can be introduced readily into a benzene ring which contains an hydroxyl group. As usual, the hydroxyl group sends the entering radical to the para position. In the case of phenol, over 95 per cent of the oxydiphenyl obtained was the para compound. About 5 per cent of an isomer was obtained which, in all probability, was the ortho compound. The substance was not obtained in quantity sufficient to warrant a determination of its structure. In the reaction the hydrogen atom of the hydroxyl group is, to some extent, replaced by phenyl, and an ether results.

The decomposition of benzenediazonium chloride with pyrocatechin proceeded in the same general way. The chief reaction-product was a dioxydiphenyl. The substance formed in the next largest amount was shown to be *o*-oxyphenyl ether, which was formed by the replacement of a hydrogen atom of one of the hydroxyl groups by phenyl. A very small quantity of a substance, which was evidently an isomer of the dioxydiphenyl obtained, was also isolated.

In resorcin there is one position in the benzene ring which is para to one hydroxyl group and ortho to the other. As the orienting influence of both groups is thus, at the same time, directed to this place, it seemed that in this case the reaction would be a smooth one and that isomeric compounds would not be formed. The results of the experiments were surprising, therefore, when it was found that no diphenyl derivatives could be isolated. The only product which was found was the azo compound, notwithstanding the fact that the reaction was carried out at 100°.

Preliminary experiments only have been carried out with hydroquinone. These indicate that the reaction proceeds in a manner analogous to that with pyrocatechin. The chief product of the reaction in this case appears to be *p*-oxyphenyl ether and not a diphenyl derivative, however. This differ-

ence is due, no doubt, to the fact that there is no vacant position para to an hydroxyl group, and, as a consequence, the hydroxyl hydrogen is replaced to a larger extent than is the case with pyrocatechin. To some extent, however, a phenyl group is introduced into the ring and a dioxydiphenyl is formed.

The introduction of a phenyl group into the ring in pyrocatechin and hydroquinone modifies the properties of these compounds. The resulting substances show the reactions of the simpler benzene derivatives, but their reactivity is greatly increased. For example, the phenyl derivative of hydroquinone is oxidized by atmospheric oxygen to a dark-blue compound, which can be reduced by sulphur dioxide to a colorless substance.

The ethers produced in the reaction are stable, and do not reduce an ammoniacal solution of silver nitrate.

The number of hydroxyl groups in the compounds was determined by preparing the acetyl derivatives. In some cases the methyl ethers were also made.

The descriptions of the compounds prepared from hydroquinone will be given in a subsequent paper.

Experimental.

Decomposition of Benzenediazonium Sulphate with Phenol.

The decomposition of benzenediazonium sulphate with phenol was carried out under a variety of conditions. The method finally adopted was as follows : The diazo compound was prepared by treating a cold solution of aniline sulphate, made by dissolving 40 grams of aniline in a mixture of 80 grams of sulphuric acid and 40 cc. of water, with a solution of 36 grams of sodium nitrite in 80 cc. of water. The cold solution was then poured in small portions, with constant shaking, into a large flask containing 80 grams of phenol, which was heated on a boiling water-bath. During the reaction a heavy black oil separated, and much nitrogen was evolved. In order to separate the products of the reaction, the mixture was distilled with steam and the distillate was collected in fractions. In the first experiment ordinary steam

was used and 14 fractions of 100 cc. each were collected. The first nine fractions were found to contain the excess of phenol: In fractions 10 to 14 there were a few needle-shaped crystals which melted at 67°.5 and proved to be *o*-oxydiphenyl. As the major part of the reaction-product was only slightly volatile with ordinary steam, the product of a second decomposition was distilled with superheated steam. The oil formed in the reaction was separated and put into a 500 cc. flask, which was heated to 150° in an oil-bath. The steam, after passing through a ⅜-inch iron pipe heated in a 30-inch combustion furnace, was at a temperature of 140° to 160°, when it entered the flask. Under these conditions all the oxydiphenyl had distilled over when 700 cc. of water had been collected. The distillate was collected in fractions of 50 cc. each. Numbers 1 to 5 contained an oil, 6 and 7 a semi-pasty mass, and 8 to 14 a white solid. The oil contained the excess of phenol and some *o*-oxydiphenyl, fractions 6 and 7 consisted of a mixture of the ortho and para compounds, and the white solid was almost pure *p*-oxydiphenyl.

The phenol recovered from the first fractions of the distillate weighed 44 grams. Thirty-six grams had, therefore, entered into reaction with the diazo compound, whereas the theoretical quantity required by the following equation for the aniline used is 40 grams :

$$C_6H_5.N_2SO_4H + C_6H_5OH = C_6H_4.C_6H_4OH + H_2SO_4 + N_2.$$
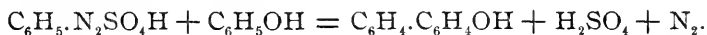
The separation of the isomeric oxydiphenyls was best effected by crystallization from hot petroleum ether (b. p. 50° to 80°) in which the para compound is only slightly soluble in the cold, and in which the ortho compound is much more soluble both hot and cold. *p*-Oxydiphenyl crystallizes well from hot 20 per cent alcohol.

As a result of the decomposition, there was obtained from 40 grams of aniline, 20 grams of pure *p*-oxydiphenyl and 1.5 grams of the isomer. There was a large amount of the reaction-product which was not volatile with steam. It consisted of a black, brittle mass, which dissolved in sodium hydroxide and was precipitated from this solution by the addition of hy-

drochloric acid. The mixture probably contained substances which were formed by the introduction of more than one phenyl group into the benzene ring.

Hirsch noted that an isomer of *p*-oxydiphenyl is formed in the decomposition of benzenediazonium salts with phenol, and assigned to it the ortho structure. No analyses are reported and the properties of the compound are not given. The amount of material obtained by us was not sufficient to warrant an investigation of the structure of the compound. It is, in all probability, an ortho substitution-product produced as a result of the well-known orienting influence of the hydroxyl group. An analysis of the compound melting at $67°.5$ resulted as follows :

0.1308 gram substance gave 0.4047 gram CO_2 and 0.0700 gram H_2O.

	Calculated for $C_{12}H_{10}O$.	Found.
C	84.71	84.31
H	5.88	5.91

The compound crystallizes in colorless needles, which are stouter than those of the para compound.

Decomposition of Benzenediazonium Chloride with Pyrocatechin.

As the result of a preliminary experiment it was found that the chief products of the reaction between benzenediazonium salts and pyrocatechin were dioxydiphenyl, *o*-oxydiphenyl ether, and an oil which could not be distilled without decomposition. Of a number of methods of separating the mixture into its constituents which were studied, the one described below was found to be the best.

The diazo compound was prepared by treating a solution of 40 grams of aniline in 100 grams of concentrated hydrochloric acid diluted with 100 cc. of water, with 32 grams of sodium nitrite dissolved in 80 cc. of water. This solution was poured very slowly into a mixture of 50 grams of pyrocatechin and 50 cc. of water, which was heated to about $75°$. The product was distilled with steam and the distillate collected in fractions. The first fractions, which contained an oil, were extracted with ether, from which 6.5 grams of phenol were ob-

tained. The solid volatile with steam was found to be *o*-oxy-diphenyl ether. About 4 liters of water were necessary to carry over the phenol and the 4.6 grams of ether formed in the reaction. The solution in the flask was decanted from the non-volatile oil and evaporated to a small bulk. The dioxy-diphenyl which separated was filtered off, and from the filtrate 21 grams of pyrocatechin were recovered. Thirty-nine grams had, therefore, entered into reaction instead of 47 grams—the theoretical quantity for a reaction between an equal number of molecules of the diazo compound and the phenol.

The non-volatile oil was extracted three times with boiling water. In all, 2.5 liters were required to dissolve the dioxy-diphenyl. On cooling, 5 grams of the compound crystallized out and 4 grams in addition were obtained on evaporation. The oil insoluble in water weighed 10 grams. It dissolved in alkali, however, and was, no doubt, a mixture of complex phenols formed by the introduction of more than one phenyl group into the pyrocatechin molecule. An attempt was made to distil this oil. After about 1 gram of a colorless substance had distilled over at 220° to 250°, total decomposition took place. The distillate, after crystallization from a mixture of toluene and petroleum ether, melted at 147°.5 to 148°.5. The substance reduced silver nitrate, gave a white precipitate with lead acetate, and produced a light-green color with ferric chloride, which changed to a reddish-brown on standing and to a deep-violet on the addition of sodium carbonate. The compound was evidently a pyrocatechin derivative, and probably an isomer of the dioxydiphenyl formed as the chief product of the reaction.

The reaction between benzenediazonium salts and pyrocatechin was brought about in a number of ways, in order to determine the effect of the conditions on the yield of the various products of the reaction. The decomposition was effected by raising gradually the temperature of a mixture of the diazo compound and the phenol, by bringing about the reaction at different temperatures, and at 75° and at 100° in the presence of copper powder. In no case were the yields as good as in the experiment described above.

o-Oxydiphenyl Ether.—About 4.6 grams of this substance were obtained from 40 grams of aniline. The compound crystallizes from dilute alcohol in flat needles, and from petroleum ether in well-formed, six-sided needles terminated by domes. It is slightly soluble in hot water, from which it separates, on cooling, in long needles. A cold saturated solution contains 0.11 gram to the liter. *o*-Oxydiphenyl ether melts at 105° to 106° and has an aromatic odor. It is very soluble in carbon bisulphide, benzene, and glacial acetic acid, less soluble in toluene, and only slightly soluble in petroleum ether. It gives no color with ferric chloride, and shows none of the characteristic reactions of pyrocatechin. The results of an analysis follow :

0.1105 gram substance gave 0.3125 gram CO_2 and 0.0553 gram H_2O.

	Calculated for $C_{12}H_{10}O_2$.	Found.
C	77.42	77.08
H	5.37	5.56

A molecular-weight determination, using alcohol as the solvent, gave 176 as the result instead of 186, the theoretical number.

The acetyl derivative was made by heating the phenol with an excess of acetyl chloride. After the product so obtained had been treated with sodium hydroxide it distilled without decomposition at 358° to 360° (uncorr.). The compound is a thick oil, which dissolves in the usual organic solvents. An analysis gave the following results :

0.1251 gram substance gave 0.3386 gram CO_2 and 0.0607 gram H_2O.

	Calculated for $C_{14}H_{12}O_3$.	Found.
C	73.68	73.82
H	5.26	5.39

The methyl ether of *o*-oxydiphenyl ether was prepared by heating a solution of the phenol in methyl alcohol with the calculated quantities of potassium hydroxide and methyl iodide. The compound crystallizes from methyl alcohol in long, flat, six-sided crystals. It dissolves in the ordinary sol-

vents and melts at 77°.   The formation of this compound and
of the monoacetyl derivative described above, shows that the
structure assigned to the *o*-oxydiphenyl ether is correct.   An
analysis of the methyl ether gave the following results :

0.1074 gram substance gave 0.3063 gram CO_2 and 0.0589
gram H_2O.

	Calculated for $C_{13}H_{12}O_2$.	Found.
C	78.00	77.78
H	6.00	6.09

Dioxydiphenyl.—Nine grams of this compound were ob-
tained from 40 grams of aniline.   The crude substance which
was separated from the original reaction-product by extraction
with water was dark-brown in color and somewhat gummy.
In this condition it is best purified by crystallization from hot
petroleum ether, in which it is only slightly soluble.   It melts
at 136° to 136°.5 and boils above 360° without decomposition.
It is very soluble in alcohol, chloroform, and ether, less solu-
ble in carbon bisulphide, petroleum ether, and hot water.   A
cold, saturated, aqueous solution contains 1.6 grams per liter.
The compound gave a light-green color with ferric chloride,
which changed to a reddish-brown on standing, and which
was changed to a deep-violet on the addition of sodium car-
bonate.   It reduces silver nitrate, and gives a precipitate with
lead nitrate and with bromine water.   No marked coloration is
produced when the substance is heated with phthalic anhy-
dride and sulphuric acid.   An analysis gave the following re-
sults :

0.2048 gram substance gave 0.5826 gram CO_2 and 0.1022
gram H_2O.

	Calculated for $C_{12}H_{10}O_2$.	Found.
C	77.42	77.53
H	5.37	5.54

The diacetyl derivative was obtained by heating the phenol
with an excess of acetyl chloride.   It crystallizes from alcohol
in long, six-sided crystals, which melt at 77° to 77°.5.   The
analytical results were as follows :

0.1285 gram substance gave 0.3341 gram CO_2 and 0.0628 gram H_2O.

	Calculated for $C_{16}H_{14}O_4$.	Found.
C	71.11	70.91
H	5.18	5.43

Two dioxydiphenyls are possible as the result of the introduction of a phenyl group into the benzene ring of pyrocatechin. In one compound the group introduced is ortho and meta to the two hydroxyl groups; in the other it is para and meta to these groups. An attempt was made to determine which of these structures belonged to the dioxydiphenyl formed as the chief product of the decomposition of the diazonium salt with pyrocatechin. The phenol was converted into the corresponding dimethyl ether, which was then oxidized. It was expected that in this way the phenyl group would be converted into carboxyl and, as a result, a dimethoxybenzoic acid obtained. If the phenyl group occupied the position para to one of the hydroxyl groups, the oxidation-product would be veratric acid, a well-described compound. The oxidation was brought about under a variety of conditions with chromic acid and with potassium permanganate. Only when the last-named substance was used could any oxidation-product be isolated, which in this case proved to be benzoic acid. The structure of the compound was not established, therefore, but on account of the usual directing influence of the hydroxyl group and the results with phenol, it is highly probable that the substance is 3,4-dioxydiphenyl.

BOSTON, MASS., Nov. 1, 1902.

XXXIX.—THE ACTION OF ZINC ON TRIPHENYL-CHLORMETHANE.

BY JAMES F. NORRIS AND LLORA R. CULVER.

In an investigation of some new applications of the Friedel and Crafts reaction, which was carried out in this laboratory nearly four years ago, the condensation of carbon tetrachloride with benzene was studied under conditions different from those which had been used in the past. It was thought that

the change in conditions might lead to the formation of tetra-
phenylmethane, instead of triphenylmethane, the compound
which had been obtained as the product of this reaction.   The
substance formed, however, proved to be triphenylchlormeth-
ane.[1]   As the compound could be obtained readily in this
way in a high state of purity, and as it proved to be a very
reactive substance of unusual interest, we undertook a thor-
ough study of it and its reactions.   Among the experiments
undertaken was an attempt to condense the compound with
brombenzene by means of sodium, and thus prepare tetra-
phenylmethane.   We obtained, as the result of the reaction,
not the expected product but a compound containing oxygen.
This substance and the cause of its formation were under in-
vestigation when papers appeared by Gomberg[2] on the prepa-
ration of triphenylchlormethane, and the action of metals on
this compound.   As our work was well in hand at this time,
a preliminary paper was published from this laboratory out-
lining what had been done and what was under investigation
at that time.   This was thought to be advisable, as our re-
sults in part supplemented those of Gomberg.   We had iso-
lated an intermediate compound in the preparation of tri-
phenylchlormethane from carbon tetrachloride, which had not
been obtained by Gomberg.   This substance, which has the
formula $Al_2Cl_6.2(C_6H_5)_3CCl$, appeared of interest as it was the
first compound of aluminium chloride with an alkyl chloride
to be isolated.   It has proved of interest since its discovery.
It was also shown in the same paper that, under certain con-
ditions, triphenylchlormethane reacts with sodium, contrary
to the observations of Gomberg.[3]   This paper was replied to
by Gomberg,[4] who claimed priority and disputed our right to
continue our line of work.

　　The brilliant discovery by Gomberg of the highly unsatu-
rated compound formed by the action of zinc on triphenyl-
chlormethane, led to conclusions as to the structure of the
substance which were at variance with the accepted views of

[1] This JOURNAL, **25**, 54.
[2] J. Am. Chem. Soc., **22**, 752, 757.
[3] *Ibid.*, **22**, 758.
[4] *Ibid.*, **23**, 109.

the valence of carbon. As the unsaturated compound was of such unusual interest, we continued our investigation to discover if any explanation of the remarkable reaction, other than that of trivalent carbon, could be found. We did this as the point did not appear to us to be proved, and as our own experiments had put us in a position where we could go on with the work started before Gomberg's first paper appeared.

In a second paper by one of us,[1] the view was put forward tentatively that the unsaturated compound had the structure $(C_6H_5)_2C = C_6H_4$, it being formed by the elimination of hydrogen chloride from triphenylchlormethane. As evidence for this view, the statement was made that when zinc reacted with triphenylchlormethane dissolved in ethyl acetate, hydrogen was evolved. It was shown that zinc had no action on ethyl acetate and, consequently, the hydrogen must come from the triphenylchlormethane.

In a reply to this paper it was pointed out by Gomberg[2] that, when ethyl acetate which had been dried over phosphorus pentoxide was used in the reaction, no hydrogen was evolved, but that when the solvent was dried in the usual way over calcium chloride, the gas was formed. The observed evolution of hydrogen was due, as a consequence, to the action of the water present on the triphenylchlormethane, by which hydrochloric acid was liberated. This acid, in turn, reacted with the zinc to form hydrogen. This work of Gomberg showed that the experimental evidence put forward by one of us was faulty, in that care had not been taken to use an absolutely dry solvent.

The study of the action of metals on triphenylchlormethane was continued, nevertheless, as the work which had already been done had brought to light a number of facts overlooked by Gomberg, which needed explanation. With the view of testing every hypothesis that suggested itself before accepting the explanation of trivalent carbon, an attempt was made to determine quantitatively the substances which entered into the reaction and the products formed.

[1] This JOURNAL, **25**, 117.
[2] *Ibid.*, **25**, 317.

At the beginning of the work it was found that the statement of Gomberg[1] was incorrect, that when the reaction between zinc and triphenylchlormethane took place in benzene solution, the metal reacted quantitatively according to the following equation :

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C— + ZnCl_2.$$
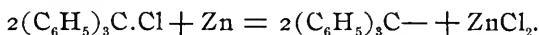
During the course of the reaction a thick, dark mass separates, which Gomberg assumed to be a compound of benzene and zinc chloride. In determining the amount of chlorine removed by the metal, this mass was shaken with water and the halogen determined. The amount found was equal to that in the triphenylchlormethane used. From this the conclusion was drawn that all the chlorine was in the form of zinc chloride. In our earliest experiments we found that zinc chloride, like aluminium chloride, forms a compound with triphenylchlormethane, and that the dark, gummy mass formed in the reaction consisted in part of this compound, for when it was decomposed with water, triphenylcarbinol was set free. The single quantitative experiment on which Gomberg based his theory in his first paper was, therefore, manifestly incorrect, and there were no data as to the amounts of zinc and triphenylchlormethane which entered into reaction. Gomberg, in a later paper, briefly mentioned this mistake, but he has reported no further work to test this point.

When a solution of triphenylchlormethane in ethyl acetate is treated with zinc, care being taken to exclude oxygen, a highly unsaturated compound is formed, which readily absorbs oxygen and is thus converted into an insoluble peroxide of the formula $(C_6H_5)_3C—O—O—C(C_6H_5)_3$. The amount of this compound formed, according to Gomberg, varies usually between 75 and 80 per cent of the theoretical amount calculated from the triphenylchlormethane used. The filtrate from the peroxide, which contains about one-fourth of the organic reaction-product, has not received in the past the attention that it deserves. As triphenylmethane, triphenylcarbinol, and an oil are at times present, an investigation of the cause of the formation of these substances must be made before the reac-

[1] J. Am. Chem. Soc., **22**, 761.

tion, which is evidently a very complex one, can be exactly interpreted.

The substances mentioned above were found in the filtrate when precautions were taken to avoid the presence of moisture during the reaction between the zinc and the organic halide. Triphenylchlormethane was converted in part into triphenylmethane. It was important to discover, if possible, whence came the hydrogen that had replaced the chlorine. It is possible that a reaction might take place according to the following equation :

$$2(C_6H_5)_3CCl + Zn = (C_6H_5)_2C{=}C_6H_4 + (C_6H_5)_3CH + ZnCl_2.$$
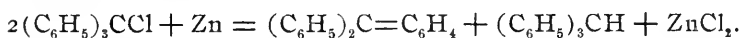
Such a reaction would be analogous to that between zinc and another tertiary halide :

$$(CH_3)_3CI + Zn = (CH_3)_2C{=}CH_2 + (CH_3)_3CH + ZnI_2.$$
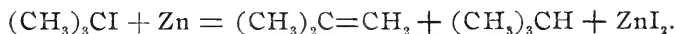
Some time ago Nef[1] studied the action of zinc on triphenylbrommethane. In all the experiments reported, triphenylmethane was the chief product of the reaction. An amorphous substance was also formed. Nef explained the reaction by assuming that the metal caused the elimination of hydrobromic acid from triphenylbrommethane, and that an unstable compound of the formula

$$(C_6H_5)_2\underset{\downarrow}{C}{-}\underset{\downarrow}{C}_6H_4$$
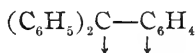
was produced. This substance was reduced in part to triphenylmethane and in part converted by polymerization into a red tar. When 5 grams of the bromide dissolved in 20 cc. of absolute ether were treated with 2 grams of granulated zinc at 65°, 1.6 grams of triphenylmethane were obtained.

As a determination of the amount of triphenylmethane formed in our experiments showed that but small quantities were present, it was evident that the main reaction was not that written above. It is highly probable that the reaction described by Nef does take place to some extent, even at room temperature, and that, in this way, the triphenylmethane and the oil noted above were produced.

[1] Ann. Chem. (Liebig), **309**, 169.

Nef's experiments were carried out at temperatures varying from 65° to 150° where polymerization of the compound

$$(C_6H_5)_2C=C_6H_4$$
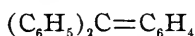
probably took place.   As it seemed that such a compound might be capable of existence at room temperature, and might prove to be the triphenylmethyl of Gomberg, an attempt was made to remove hydrogen chloride from triphenylchlormethane without the use of heat.   To this end the halogen compound was treated with pyridine, as it is claimed that this compound readily removes hydrogen chloride from acetyl and benzoyl chlorides.

Five grams of triphenylchlormethane and 1.42 grams of pyridine were dissolved in a small quantity of ethyl acetate and set aside.   At the end of a few days large, pink crystals, which melted at 167° to 167°.5, had separated.   These were washed with ether, dried at 105°, and analyzed.   The percentages of chlorine in two different samples were 10.05 and 9.72, respectively.   The theoretical for a compound of the formula $(C_6H_5)_3CCl.C_6H_5N$ is 9.93 per cent.   The compound does not lose weight over sulphuric acid, and is decomposed by water with the formation of triphenylcarbinol and pyridine.

The experiment did not lead to the desired result.   Nef had previously removed hydrogen bromide from triphenylbrommethane by means of triethylamine, but the reaction was carried out in boiling benzene and a tar was produced.

While the work of Nef furnishes an explanation of the manner in which triphenylmethane is produced in the reaction, no experimental work so far reported has furnished any explanation of the formation of triphenylcarbinol.   As this substance is formed in appreciable quantities, the reaction between zinc and triphenylchlormethane cannot be correctly interpreted until the presence of the carbinol is explained.   A study of the quantities of zinc and triphenylchlormethane which entered into the reaction, and the amount of oxygen absorbed by the unsaturated compound produced, furnished a reasonable explanation of this point.

In making a quantitative study of the reaction a special piece of apparatus was used. A 30 cc. Erlenmeyer flask was fitted with a rubber stopper through which passed two tubes bent at two right angles. These tubes were connected by means of heavy rubber tubing to two Hempel gas burettes containing mercury. By raising and lowering the side tubes, the gas confined could be passed from one burette, through the flask, into the other burette. In order to prevent any leak at the joints, there were fitted to the burettes and the neck of the flask, by means of rubber stoppers, pieces of glass tubing of large diameter. These tubes were placed in such positions that they formed cups around the rubber connectors. The cups were then filled with mercury which completely covered the joints. During an experiment the enclosed gas was kept under a slightly reduced pressure, as an inward leak of gas was impossible. A layer of concentrated sulphuric acid, which floated on the surface of the mercury in one of the burettes, served to dry the gas admitted.

In performing an experiment, the burettes were partially filled with oxygen and a weighed quantity of carefully purified triphenylchlormethane was placed in the small flask. A measured quantity of ethyl acetate, which was free from acid, water, and alcohol, was next added. A small glass tube containing a weighed quantity of pure granulated zinc was then introduced into the flask. The tube was flat on the bottom so that it stood in the liquid and thus prevented the contact of the metal with the ethyl acetate. The flask was next connected with the burettes by means of the stopper, and the outside glass jacket put into place and filled with mercury. When all was tight, the gas enclosed in the apparatus was passed through the flask from one burette to the other. In this way it was dried by coming in contact with the sulphuric acid and became saturated with ethyl acetate vapor. Readings of the temperature and volume were made until a constant state of affairs had been reached. The flask was now carefully shaken, the tube containing the zinc was overturned, and the metal thus brought into contact with the solution. Reaction set in immediately, and the solution assumed a dark-

yellow color. In a short time the peroxide began to separate. The rate of absorption of the oxygen was noted by frequent readings of the volume of the gas. At first the gas was absorbed quite rapidly, but toward the end of the experiment the absorption was very slow. The yellow color of the solution slowly decreased until it had almost entirely disappeared, when the reaction was complete. When the absorption ceased, the flask was removed and the zinc left was determined. It was not found difficult to separate the metal from the precipitated peroxide. The small amount of this substance which adhered to the zinc was removed by dissolving it in hot carbon tetrachloride. The difference in the weight of the zinc before and after the reaction was evidently the amount which had entered into the reaction. The weight of the peroxide formed in the reaction was also determined. The precipitate was filtered from the reaction-mixture and washed with a little ethyl acetate, in which it is not appreciably soluble. The part removed from the zinc by carbon tetrachloride was recovered and added to the main amount. As zinc oxide was found to be a product of the reaction, and as it was collected with the peroxide, the latter was weighed, then treated with hydrochloric acid, and weighed again. These data gave the amounts of peroxide and zinc oxide formed.

The original filtrate from the peroxide, which contained the products of the reaction soluble in ethyl acetate, was diluted with ether, shaken with water to remove zinc chloride, and evaporated to dryness. In all cases triphenylcarbinol and a small quantity of an oil were formed. In some cases triphenylmethane was also found. When this was the case the filtrate was much richer in oil, which had a pleasant aromatic odor. The mixture left on evaporation was dissolved in benzene from which the carbinol and the triphenylmethane crystallized. When the solution had gone to dryness the crystals were removed and pressed on an absorbent plate in order to free them from the oil. The crystals were then washed with a little cold benzene. To separate the hydrocarbon from the carbinol the mixture was treated with concentrated sulphuric acid in which the carbinol is soluble. The carbinol is pre-

cipitated by diluting the acid solution with water. The part insoluble in the acid was crystallized from benzene, and was identified as triphenylmethane by the melting-point of the crystals formed, and the change in their melting-point when crystallized from alcohol. The carbinol was readily obtained in pure condition by crystallizing it from carbon tetrachloride. The oily product of the reaction was obtained in very small quantities, and as it was evidently a mixture it was not investigated.

A series of experiments was also made in which the oxygen absorbed was not determined. In this case the flask in which the reaction was carried out was closed by a cork carrying a drying-tube. The results of a number of experiments are tabulated below. In the columns marked "theoretical zinc" and "per cent zinc used" are given the amount required by Gomberg's equation :

$$2(C_6H_5)_3CCl + Zn = 2(C_6H_5)_3C- + ZnCl_2.$$
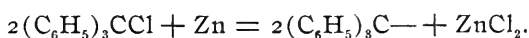
No.	$(C_6H_5)_3CCl$ used.	Zn used.	Theoretical zinc.	Per cent Zn used.	Per cent peroxide obtained.	Oxygen in peroxide.	Oxygen used.	Weight of product in filtrate.
1	2.721	0.369	0.318	116	52	0.081	0.116	1.044
2	1.091	0.252	0.127	198	29	0.018	0.061	0.637
3	1.940	0.329	0.226	145	48	0.053	0.100	0.875
4	2.121	0.417	0.248	169	38	0.046	0.098	1.183
5	1.470	0.218	0.172	127	70	. . . .	. . . .	0.407
6	2.084	0.353	0.243	145	53	. . . .	. . . .	0.863
7	1.091	0.165	0.127	130	37	. . . .	. . . .	0.624
8	1.013	0.225	0.118	190	35	. . . .	. . . .	0.649
9	1.090	0.171	0.127	135	49	. . . .	. . . .	0.525

An examination of the results shows that the reaction between zinc and triphenylchlormethane is a very complicated one and that very slight changes in the conditions of the experiment have a marked influence on the result. The most evident facts are, first, that much more zinc is used than is called for by Gomberg's equation ; second, that much more oxygen is absorbed than is contained in the peroxide ; and

third, that the percentage of peroxide obtained is less than that found by Gomberg. These quantitative results must be interpreted before the nature of the reaction between zinc and triphenylchlormethane can be understood.

An explanation of the large amount of zinc used suggests itself. The usual action of zinc on alkyl halides is of the nature of that represented by the following equations :

$$C_2H_5I + Zn = C_2H_5{-}Zn{-}I \; ;$$
$$2C_2H_5{-}Zn{-}I = Zn(C_2H_5)_2 + ZnI_2.$$
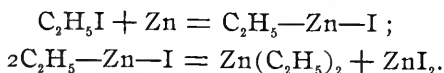
In this case 1 molecule of the halide reacts with 1 atom of zinc. In Gomberg's equation, 2 molecules react with 1 atom of zinc. If the formation of a zinc alkyl took place completely in the case of triphenylchlormethane, twice the amount of zinc calculated from Gomberg's equation would be used. If it took place in part in this way and in part according to Gomberg's explanation, the amount of metal used would be between 100 and 200 per cent. For some time we have been studying in this laboratory the action of metals on a number of halogen derivatives, and have found that zinc forms compounds with a number of chlorides. It is possible that it may form to some extent a zinc alkyl with triphenylchlormethane. Such a compound would no doubt be a very reactive substance.

Zinc ethyl reacts with oxygen to form the compounds :

$$\begin{array}{c} C_2H_5O\!\diagdown \\ {\diagup}Zn \\ C_2H_5 \end{array} \qquad \text{and} \qquad \begin{array}{c} C_2H_5O\!\diagdown \\ {\diagup}Zn. \\ C_2H_5O \end{array}$$
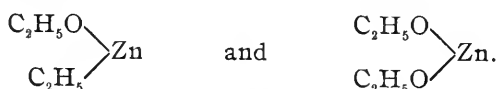
The first of these compounds decomposes with water into zinc hydroxide, ethane, and alcohol. The second gives zinc hydroxide and alcohol. If a zinc alkyl is formed with triphenylchlormethane, or if the intermediate compound

$$(C_6H_5)_3C{-}Zn{-}Cl$$
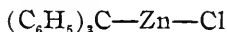
is produced, it would probably absorb oxygen and be converted into a substance which, on further decomposition, would yield triphenylcarbinol.

This explanation of the formation of triphenylcarbinol,

which was found in the filtrate in every experiment, also serves to explain the fact that much more oxygen is absorbed than is contained in the peroxide. In experiment No. 2, for example, 0.061 gram of oxygen were used, whereas the peroxide found contained only 0.018 gram. In this experiment the carbinol formed was determined. The amount of oxygen in this compound was 0.0392 gram. The sum of the oxygen in the peroxide and carbinol was, accordingly, 0.0575 gram, which is a little less than the total amount used, 0.0609 gram. This relation held in the other experiments, the sum of the oxygen in the peroxide and the carbinol being nearly equal to the total oxygen used. It seems highly probable, therefore, that the carbinol formed in the reaction is produced as a result of the action of oxygen on some unstable compound in solution.

If a zinc alkyl is formed as suggested here, zinc hydroxide would be one of the products of its decomposition. This compound was shown to be present in some of the experiments. The amounts obtained varied between 0.007 and 0.047 gram.

The fact that the yield of peroxide obtained by us is much less than that obtained by Gomberg is a striking one. According to Gomberg a low yield of peroxide, when ethyl acetate is used as a solvent, is due to the presence of water or alcohol which causes the decomposition of the triphenylchlormethane with the formation of hydrochloric acid. This explanation does not apply to our results, as no hydrogen was evolved as the result of the action of the liberated acid on the zinc. If the gas had been given off, in the apparatus used by us, it could not escape and, consequently, it would have been measured with the enclosed oxygen. The decrease in the volume of gas, which was taken as a measure of the oxygen absorbed, would have been, accordingly, smaller than it should have been. The experimental results are in just the opposite direction, however. As the percentage of peroxide obtained decreased, the ratio of the oxygen absorbed to the peroxide increased. The results also show that as the amount of zinc used increases, the amount of peroxide formed decreases. The high percentage of zinc used was accompanied also by a

high percentage of carbinol. If it is assumed that a zinc alkyl is formed, these facts indicate that an increase in the quantity of the alkyl is accompanied by a decrease in the amount of peroxide and an increase in the amount of carbinol. We must conclude, therefore, that the hypothetical zinc alkyl is not the compound from which the peroxide is produced by the action of oxygen. The carbinol, however, is probably formed in this way.

A quantitative study of the reaction between triphenylchlormethane and zinc, carried as far as could be done conveniently, does not serve to answer definitely the question as to the structure of the highly unsaturated compound discovered by Gomberg. The work done throws a great deal of light on the reaction and proves that it is of a very complex nature. The facts brought forward do not prove or disprove the correctness of the conception of trivalent carbon, but where so many reactions are taking place simultaneously there is a chance that there may be subtle changes going on which the experimental data, so far collected, do not lead us to suspect. It must be said, however, that none of the facts can be used as evidence against the existence of triphenylmethyl. The equation written by Gomberg may express a part of the truth, but evidently another reaction of importance is also involved. It is also probable that the reaction which leads to the formation of the carbinol takes place more readily in ethyl acetate than in benzene solution. This investigation was carried out with ethyl acetate as solvent, as the products of the reaction are soluble in the acetate. When benzene is used, the separation of a compound containing triphenylchlormethane complicates the study of the reaction.

Work is now in progress to test the view already put forward by one of us that a hydrogen atom in a benzene ring is involved in the reaction. The investigation will be continued along this line, as the experimental evidence put forward in support of the view that the unsaturated compound from which the peroxide is formed contains a trivalent carbon atom, does not appear to the writer sufficient to warrant the acceptance of such a radical assumption.

BOSTON, MASS., Dec. 1, 1902.

XL.—THE ACTION OF ZINC ON BENZOYL CHLO-RIDE.

By James F. Norris and D. R. Franklin.

The great importance of correctly interpreting the reaction that takes place between zinc and triphenylchlormethane has led us to study the action of the metal on a number of organic halogen compounds. An examination of the literature brings out the fact that at times zinc causes a simple condensation by removing 2 atoms of the halogen from 2 molecules of the organic compound. In some cases an unstable zinc alkyl is formed. In other cases the zinc compound produced is stable. Very often the metal causes the elimination of halo-gen hydride and complex condensations result.

The reactions as studied in the past have been carried out at elevated temperatures when the zinc chloride produced in the reaction has a marked effect. It seemed probable that a review of some of the older work in this field might lead to new facts of importance which would serve to explain the re-sults of work already reported and to throw some light on the important reaction, the study of which has led to such inter-esting results and conclusions.

Among the reactions studied is that which takes place be-tween zinc and benzoyl chloride. This work was undertaken on account of the analogy between benzoyl chloride and tri-phenylchlormethane. At first sight the similarity between these compounds may not appear, as one is an acid chloride, whereas the other is an alkyl chloride. This difference is more one of name than of fact. A study of the reactions of triphenylchlormethane shows that the compound resembles an acid chloride, notwithstanding the fact that its structure indicates no analogy. Triphenylchlormethane reacts readily with water and is thus converted into a hydroxyl compound. With alcohol it reacts as an acid chloride, and the chlorine is replaced by an ethoxyl group. The resulting compound, al-though an ether in structure, is readily decomposed. The analogy between benzoyl chloride and triphenylchlormethane

is indicated by writing the structures of the compounds as follows :

$$C_6H_5C \overset{\displaystyle O}{\underset{\displaystyle Cl}{<\!\!\!\!\!<}} \qquad\qquad C_6H_5C \overset{\displaystyle (C_6H_5)_2}{\underset{\displaystyle Cl}{<\!\!\!\!\!<}}$$

In the triphenylmethane derivative we have two phenyl groups in place of an oxygen atom. Two phenyl groups are not as negative as an oxygen atom and we would expect, therefore, to find some differences between the reactions of the compounds. The reactivity of the chlorine atom in compounds built on the above type is, no doubt, dependent on the nature of the radicals to which the halogen is joined. For example, when we replace two hydrogen atoms in ethyl

chloride, $CH_3.C \overset{\displaystyle H_2}{\underset{\displaystyle Cl}{<\!\!\!\!\!<}}$, by a negative oxygen atom, $CH_3C \overset{\displaystyle O}{\underset{\displaystyle Cl}{<\!\!\!\!\!<}}$,

we change in a most marked degree the reactivity of the chlorine atom. By the change, we increase the negative character of the molecule to such an extent that the compound becomes unstable and readily exchanges its chlorine for a less negative hydroxyl group. It seems to the writer that the positive or negative character of the group to which a chlorine atom is joined is the main factor which determines the degree of reactivity of the halogen with other compounds. The difference, therefore, between an acid and alkyl chloride is no sharper than that between an acid- and base-forming element.

From this point of view the analogy in reaction between triphenylchlormethane and benzoyl chloride is easy to understand. The difference between the compounds is due to the fact that two phenyl groups are not the exact equivalent of one oxygen atom. If two groups could be found whose combined character equals an oxygen atom, a compound containing these groups and built on the above type would probably act exactly as benzoyl chloride does, and the hydroxyl derivative of such a radical, while having the structure of a tertiary

alcohol, would be a true acid.[1] As it is possible to vary the positive or negative nature of the phenyl group by introducing substituting atoms or groups around the ring, it is highly probable that two groups can be found whose combined action is equal to that of an oxygen atom. Such an investigation is now being carried out in this laboratory. If two such groups can be found, it is probable that we can obtain a substance analogous to carbon monoxide. Such a compound would be a methylene derivative in which there is present a stable bivalent carbon atom. The results of experiments to test the above views will be published later.

Leaving out of account the hypothesis put forward above, it is certain that the reactions of triphenylchlormethane resemble those of benzoyl chloride and, accordingly, interesting results should be obtained as a consequence of the study of the action of zinc on benzoyl chloride. From one point of view the results would be very helpful. If, in this case, the metal removes the chlorine quantitatively, according to the reaction

$$2C_6H_5.COCl + Zn = 2C_6H_5CO + ZnCl_2,$$
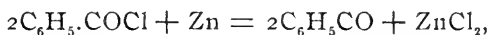
a benzoyl group would be produced. We would expect such a group to polymerize and produce dibenzoyl, a well-known compound. Gomberg's equation for the action of zinc on triphenylchlormethane is as follows :

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C— + ZnCl_2.$$
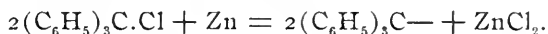
The view is put forward that the radical set free exists as such and does not double up on account of stereo-chemical considerations. The three phenyl groups take up so much room around the carbon atom that there is no chance for two such radicals to unite. The fact that no one has succeeded, in spite of much effort, in preparing hexaphenyl-

[1] From the above point of view triphenylcarbinol is a very weak acid. This conception is in accord with the view very recently put forward by Baeyer and Villiger (Ber. d. chem. Ges., **35**, 3015), who have arrived at this conclusion from an entirely different staudpoint. Gomberg (Ber. d. chem. Ges., **35**, 2397) considers the carbinol a weak base. Both conceptions are probably correct. The compound resembles to some extent the hydroxides of certain inorganic elements which are in the borderland between the well-defined acid- and base-forming elements. It is probable that by a change in the nature of the radicals the basic property of the compound can be increased to such an extent that a true carbon base will be produced.

ethane is evidence in favor of this view.[1] With benzoyl-chloride, however, this state of affairs cannot exist. Dibenzoyl is known. It was of great interest, accordingly, to see if by the action of zinc on benzoyl chloride dibenzoyl was produced, when the reaction was carried out in the absence of oxygen, and in such a way that no hydrochloric acid was given off. If benzil is produced in this way, Gomberg's view is well taken. If, however, the halogen is removed quantitatively by the metal, and benzil is not produced, the experiment is good evidence that the reaction between zinc and benzoyl chloride is of an entirely different nature from what we might expect, and that the reaction between zinc and triphenylchlormethane may not be as simple as has been supposed.

Zincke studied the action of zinc on benzoyl chloride in 1873.[2] He found that the chloride reacted violently with the metal and large quantities of hydrogen chloride were evolved. Dilution with benzene did not alter the results. Under the latter circumstances the formation of benzophenone was expected. The product of the reaction in both cases proved to be a tarry mass from which were obtained benzoic acid, a little benzophenone, and a brown substance melting at 145° to 146°, the nature of which was not established. The reaction was a violent one and led, no doubt, to deep-seated changes.

As the action of zinc on triphenylchlormethane was investigated in ethyl acetate solution (see preceding article), we studied the action of zinc on benzoyl chloride under the same conditions. Under these circumstances the temperature of the reaction-mixture did not exceed that of the room and no hydrogen chloride was evolved. A much longer time is required for the reaction to complete itself than is required in the case of triphenylchlormethane.

[1] Since the above was written Ullmann and Borsum (Ber. d. chem. Ges., **35**, 2877) have reported the preparation of a hydrocarbon by the reduction of triphenylcarbinol by means of zinc and hydrochloric acid in acetic acid solution. The evidence put forward in favor of the fact that the compound is hexaphenylethane appears satisfactory. The method of preparing the hydrocarbon was entirely analogous to that used to prepare tetraphenylethane from diphenylcarbinol. The existence of hexaphenylethane seems to the writer to be a good argument against the possibility of the existence of triphenylmethyl.

[2] Bull. soc. chim., **19**, 516 ; Ber. d. chem. Ges., **6**, 137.

Experiment 1.—As the reaction proceeded very slowly in the cold, an experiment was made to determine whether the mixture could be heated without causing any secondary reactions. A mixture of 15 grams of benzoyl chloride and 10 cc. of ethyl acetate was heated under a return condenser with a few grams of zinc chloride. The solution soon assumed a dark-brown color and a gas was given off which burned with a green flame. Evidently ethyl chloride was formed. When the reaction-product was distilled, a small quantity of acetyl chloride was obtained. The thermometer rose slowly to 249° when some benzoic acid distilled over. A charred mass was left after the volatile products had distilled off.

In an attempt to discover in what way zinc chloride brought about such a deep-seated decomposition, it was found that the chloride formed a compound with benzoyl chloride, which was very reactive. When ethereal solutions of the two substances are mixed an oil soon precipitates, which yields zinc chloride and benzoyl chloride when treated with water. This new compound reacts with a number of substances with which benzoyl chloride will not react. The important part played by zinc chloride in a number of reactions is no doubt similar to that played by aluminium chloride. In both cases the "catalytic agent" produces the final results by first forming an intermediate addition-product which is very reactive. The composition and properties of the compound of zinc chloride and benzoyl chloride and similar substances will be investigated.[1]

As a result of the above-described experiments the reaction between zinc and benzoyl chloride was allowed to take place at room temperature. It was shown that below 25° zinc chloride did not cause a reaction to take place between benzoyl chloride and ethyl acetate.

[1] Gomberg (Ber. d. chem. Ges., **35**, 2398) gives as an argument in favor of the basic character of the triphenylmethyl group the fact that its chloride forms double salts with the chlorides of certain metals. After we had shown that triphenylchlormethane formed a compound with aluminium chloride, Gomberg prepared a number of such double salts. It seems to us that the formation of such salts cannot be taken as evidence of basic properties, since such a compound as benzoyl chloride forms double salts with aluminium bromide and the chlorides of aluminium, titanium, and zinc.

Experiment 2.—A mixture of 30 grams of benzoyl chloride and 20 cc. ethyl acetate, free from alcohol, acid, and water, was allowed to stand with granulated zinc for one week. The solution was then shaken with water to remove zinc chloride and dried over anhydrous sodium sulphate. As a preliminary experiment showed that the reaction-product crystallized with difficulty, the product was distilled. After a small quantity of benzoyl chloride and benzoic acid had distilled over, the thermometer rose rapidly to 360°. When the product remaining in the flask was distilled under a pressure of 100 mm. 10 grams of an oil were obtained, which boiled at 258°. The oil soon changed to a mass of crystals which melted at 41° to 43°. On recrystallization from alcohol a melting-point of 42° was obtained. The compound was shown to be benzoic anhydride by treating it with aniline, when benzanilide was obtained. A small residue remained in the distillation-flask. No benzil—the substance expected as the product of the reaction, if the metal has caused a simple doubling up of two benzoyl groups—was obtained. The formation of benzoic anhydride could be easily explained, however. The experiment had been carried out in the presence of air. If the metal had caused the removal of the halogen from the acid chloride with the consequent formation of a benzoyl radical, this group instead of polymerizing to benzil may have absorbed oxygen and thus passed into the anhydride. The reaction would be parallel, in this case, to that which takes place, according to Gomberg, between zinc and triphenylchlormethane, the only difference being that in the case of the benzoyl group one oxygen atom is absorbed and an oxide is formed, whereas with triphenylmethyl 2 atoms produce a peroxide. With triphenylchlormethane, the hydroxyl derivative of the radical, triphenylcarbinol, is one of the products of the reaction. With benzoyl chloride, the hydroxyl derivative of benzoyl, benzoic acid is also produced. The results of this experiment show a striking analogy to those with triphenylchlormethane. To test this explanation of the course of the reaction, a quantitative experiment was next carried out.

Experiment 3.—The reaction was brought about in an apparatus in which the amount of oxygen absorbed could be measured. After standing forty-eight days, about 180 cc. of oxygen had been absorbed and 6.8 grams of zinc had passed into solution. If the reaction takes place according to the following equations,

$$2C_6H_5COCl + Zn = 2C_6H_5CO- + ZnCl_2,$$
$$2C_6H_5CO- + O = (C_6H_5CO)_2O,$$
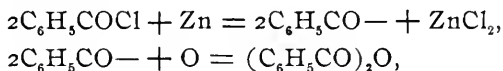
when 1 atom of zinc enters into the reaction 1 atom of oxygen will be absorbed. The quantitative results show that only about one-seventh of the oxygen required enters into the reaction. The reactions which take place are, therefore, not those written above.

The product formed in this experiment was not distilled, as it was thought that the anhydride obtained might be a secondary product formed in the distillation of the reaction-product. Further, dibenzoyl, although it distils with only slight decomposition, might undergo change under the conditions of our experiments. The product left after the evaporation of the solvent consisted of a few crystals mixed with a brown, oily substance. The crystals proved to be benzoic acid. Extraction of the mass with alcohol yielded more benzoic acid, and caused the brown substance to change to a powder which was almost insoluble in alcohol. No benzoic anhydride and no benzil were obtained. These facts confirmed the view that the anhydride was produced as the result of the destructive distillation of the original reaction-product. The brown powder could not be brought to crystalline condition. It melted at 125° to 130°. When distilled, benzoic acid and anhydride were obtained.

Experiment 4.—The relation between the amounts of zinc and benzoyl chloride which reacted with one another was next determined. Thirty grams of the acid chloride dissolved in 50 cc. of ethyl acetate were treated with an excess of zinc and allowed to stand at room temperature. After a number of days the decrease in the weight of the zinc was determined. The weighings were continued until the loss in

weight between two tests was a very small amount. At the end of thirty-two days the amount of zinc used was 100.6 per cent of the amount required according to the equation

$$2C_6H_5COCl + Zn = 2C_6H_5CO- + ZnCl_2.$$
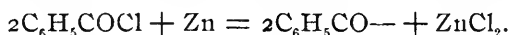
The solution of the reaction-product was washed with water and dried. One-fifth was allowed to crystallize, with the result which was obtained in the previous experiment. The remaining four-fifths, when distilled, yielded 4 grams of benzoic acid, 7.2 grams of benzoic anhydride, and 4 grams of residue. It is evident that the benzoic anhydride and a part of the benzoic acid were produced as a result of the decomposition of the brown amorphous substance, which was the main product of the reaction.

Experiment 5.—Although only a small quantity of oxygen was absorbed, it seemed possible that this amount might have prevented the polymerization of the benzoyl radical to benzil. Accordingly, the reaction was allowed to proceed in the absence of air. In this case, also, no benzil was obtained when the product of the reaction was subjected to fractional crystallization. The substances obtained were, as before, benzoic acid and the brown amorphous powder, which had no sharp melting-point. In two experiments the reaction-products were distilled. Twenty grams of benzoyl chloride, dissolved in 30 cc. of ethyl acetate, were treated with a large excess of zinc (72 grams), as it was found that the speed of the reaction was determined by the amount of the metal present. At the end of eight days the bottle containing the mixture was opened and connected with a vessel containing oxygen. About 30 cc. of the gas were absorbed. It was found that the zinc used in the reaction was 111 per cent of that required by the equation given above. When the ethyl acetate solution of the reaction-product was shaken with water to remove zinc chloride, a small amount of zinc hydroxide was formed. Upon distillation, 3.5 grams of benzoic acid and 9 grams of benzoic anhydride were obtained. In another experiment, using the same amounts of substances, the zinc which went into solution was 98 per cent of that required if the reaction is between

2 molecules of the acid chloride and 1 atom of the metal. In still another experiment, when the reaction was allowed to go on for forty-eight days, more zinc was used than is required by this ratio.

A number of unsuccessful attempts were made to obtain the chief product of the reaction, the brown amorphous solid, in a state of purity. A study of this substance would, no doubt, throw a great deal of light on the nature of the reaction.

Conclusions.

1. At room temperature zinc removes chlorine from benzoyl chloride without the formation of hydrogen chloride.

2. The molecular quantities of the two substances which react are approximately those represented by the equation

$$2C_6H_5COCl + Zn = 2C_6H_5CO- + ZnCl_2.$$
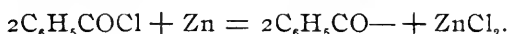
3. When the reaction is carried out in the presence of oxygen only a small quantity of the gas is absorbed.

4. When the reaction-product, after the removal of zinc chloride, is subjected to crystallization, benzoic acid and an amorphous solid are obtained. When distilled, the products obtained are benzoic acid, benzoic anhydride, and a small undistillable residue.

5. When the reaction is carried out either in the presence of, or in the absence of, oxygen no dibenzoyl is formed.

6. In some of the experiments more zinc was used than is required by the equation given above and zinc hydroxide was formed when a solution of the reaction-product was treated with water. These observations indicate that to some extent an organo-metallic compound was formed. If such a compound was produced it may have reacted with the benzoyl chloride and thus complicated the reaction. It seems probable that a study of the reaction from this point of view might lead to an explanation of the unexpected results obtained.

7. Finally, the conclusion can be drawn that the reaction between zinc and benzoyl chloride is such a complicated one that it cannot be interpreted by the use of the facts so far discovered.

BOSTON, MASS., Nov. 1, 1902.

II.—METHODS FOR THE ESTIMATION OF THE PROTEOLYTIC COMPOUNDS CONTAINED IN CHEESE AND MILK.

By Lucius L. Van Slyke and Edwin B. Hart.

When milk-casein and its salts, or paracasein, in cheese, and its salts are acted upon by dilute acids or alkalies under certain conditions, or by enzymes, or by micro-organisms, the proteid bodies are split up, forming a variety of complex cleavage-products. The extent and intensity of such proteolytic changes are measured by the proportions and kinds of the different compounds resulting from the decomposition. In the ripening process that takes place in cheese, we have an instance of extensive proteolysis in the case of the nitrogen compounds of the fresh cheese, due probably to the combined action of dilute acid, enzyme, and micro-organisms. In our study of the causes that produce cheese ripening and of the conditions that influence the process, we were at the start brought face to face with the difficulty involved in the lack of satisfactory methods for making quantitative separations and determinations of the products of cleavage formed. While we have well-elaborated methods for estimating the amount of casein and albumin in fresh milk, these are of little aid in studying the products of their decomposition. Little attention has been given to the development of methods that are applicable to the products occurring in this field. Serious difficulties are involved in such a study. First, we know at present only in an extremely meagre and vague way the chemical constitution of milk-casein and its allied compounds. As regards the constitution of the various compounds formed by the proteolysis of casein, we are largely in the dark, except in the case of some of the simpler ones. In the second place, this field is difficult to study, because the quantities of individual compounds that we have to work with are usually very small.

Under these conditions methods of quantitative separation must, at best, be regarded as largely empirical and more or

less tentative.   Instead of estimating individual compounds, about which our chemical knowledge is complete, we are compelled, in a large degree, to estimate groups of compounds, the individual members of which we know, for the most part, incompletely, or not at all.

From the peptic digestion of casein, Chitteuden has separated the proto- and deuterocaseoses,[1] and, from a tryptic digestion, a deuterocaseose and a peptone.[2]   Alexander[3] has separated heterocaseose from a peptic digestion of casein, but only in small quantities.   Many investigators have observed paranuclein or pseudonuclein, the insoluble residue remaining from the peptic digestion of casein or paracasein.   Emil Fischer and P. A. Levene[4] have obtained pyrrolidine-α-carbonic acid from a tryptic digestion of casein.

By hydrolysis of casein with hydrochloric acid, Cohn[5] obtained 1-parahydroxyphenyl-α-amidopropionic acid (tyrosine), 1-α-amidoisobutylacetic acid (leucine), amidosuccinic (aspartic) acid, α-amidoglutaric (glutamic) acid, a pyridine derivative, and ammonia.   By the same means, Emil Fischer[6] has recently isolated, among the monoamido acids, in addition to products previously obtained by others, amidovaleric acid, phenyl-α-amidopropionic acid (phenylalanine), pyrrolidine-α-carbonic acid, and probably amidoacetic acid (glycocoll).

Among the crystallizable end-products which have been found in ripening cheese are the following :   Tyrosine, leucine, histidine, α,ε-diamidocaproic acid (lysine), tetramethylenediamine (putrescine), pentamethylenediamine (cadaverine), lysatine, guanidine probably, and ammonia.   Most of these products have been recently reported by Winterstein and Thöny[7] as being found in Emmenthaler cheese.   Excepting cadaverine and guanidine, they had also been previously found, though not reported, in American cheddar

[1] Studies in Physiol. Chem., Yale Univ., **2**, 156 (1884-5).
[2] *Ibid.*, **3**, 66 (1887-8).
[3] Ztschr. physiol. Chem., **25**, 411 (1898).
[4] *Ibid.*, **33**, 170 (1901).
[5] Ber. d. chem. Ges., **29**, 1785 (1896).
[6] Ztschr. physiol. Chem., **33**, 151 (1901).
[7] *Ibid.*, **36**, 28 (1902).

cheese in this laboratory. It is very probable that other amido compounds will be found, sooner or later, among the products formed by the tryptic, if not the peptic, digestion of milk-casein and of cheddar cheese.

In cheese we find, earlier or later during the ripening process, a series of compounds and groups of compounds, which, so far as we know at present, appear in about the following order of succession : (1) Paracasein, (2) unsaturated paracasein lactate, (3) paranuclein (pseudonuclein), (4) caseoses (albumoses), (5) peptones, (6) compounds of amido acids, and (7) ammonia. After the early stages of ripeniug, we have present at the same time all these different compounds and groups.

We will consider methods for the separation and estimation of the proteolytic products found, first in cheese, and, second, in milk, following the general order indicated above. It may be well to say at the outset that, in dealing with the separation of nitrogenous bodies so complex in composition as those mentioned above and occurring in very variable quantities, we can, at present, only hope to approximate accurate quantitative results in the study of milk and cheese problems. While we have in the Nencki method a very accurate means of estimating ammonia, the methods used in separating peptones from amido compounds cannot be relied upon to give us more than approximate results.

I. METHODS FOR THE SEPARATION AND ESTIMATION OF THE NITROGEN COMPOUNDS OF CHEESE.

1. *Obtaining Sample of Cheese.*

A sample of cheese is obtained for analysis by means of a cheese-trier, which enables one to secure a round plug of cheese about 0.5 inch in diameter and 4 to 6 inches long. Four or five plugs are drawn, one within a short distance of the center of the cheese, one about an inch from the outer circumference, and the others at points equidistant between the two previously taken. Samples thus taken represent practically all different conditions existing in the cheese.

After each plug of cheese is removed, about an inch of the end having the rind is cut off and the rest placed in a well-stoppered, large-mouthed sample-bottle. The end with the rind is dipped once or twice in melted paraffin and then carefully replaced in the cheese, being pushed in a little below the surface. After all the plugs have been taken and the ends properly replaced in the cheese, some of the melted paraffin is poured over the surface to fill up and surround the depressions made by replacing the ends of the plugs. This treatment generally insures the exclusion of molds, and prevents abnormal loss of moisture in the portions of cheese near the holes left by the removal of the cheese plugs. This is a matter of much importance when one intends to keep the same cheese for one or two years for systematic examination.

When one has taken all the plugs of cheese needed, the analysis should not be long delayed. The cheese in the bottle is cut into small pieces with a spatula and stirred within the bottle, in order to mix the whole into as homogeneous a mass as possible.

2. *Determination of Total Nitrogen in Cheese.*

We weigh out 1 or 2 grams of the cheese, prepared as described above, for the determination of total nitrogen, and treat it according to the Kjeldahl-Gunning method, modified as follows : When the solution has become partially digested add a piece of copper sulphate about as large as an ordinary pea. Unless this is done it will take a long time to convert the organic nitrogen completely into ammonia.

3. *Extraction of Water-soluble Products.*

In a porcelain mortar we thoroughly mix 25 grams of our cheese sample, prepared as indicated above, with about an equal bulk of clean quartz sand. This mixture is transferred to a 450 cc. Erlenmeyer flask, to which we add about 100 cc. of distilled water at a temperature of 50° C. The flask is then placed on a water-bath, or in some place where it can be kept at a temperature of 50° to 55° C., and is allowed to stand for half an hour, being vigorously shaken from time to time. The

liquid portion is then decanted through a filter of absorbent cotton into a 500 cc. flask. The residue is again treated with 100 cc. of water, heated, agitated, and the liquid decanted as before. This process is repeated until the filtrate, after being cooled to room temperature, amounts to 500 cc., exclusive of the fat, which usually is present at the top of the liquid.

The cotton filter mentioned is made of two layers of absorbent cotton prepared as follows : In a glass funnel we place some absorbent cotton to the depth of about one inch, moisten this with water, in order to compact it, and then above this place another layer of cotton of the same thickness. Upon this we pour our portions of cheese extract. This kind of filter allows rapid filtration without the aid of a pump, and is as effective in every way as paper, which requires half a day or more for complete filtration of 500 cc. of extract. Several samples of cheese can be extracted at the same time. The upper layer of cotton holds all solid particles and can be returned to the flask for extraction with salt solution.

The method of making a water extract of cheese, as described above, insures the complete removal of all water-soluble nitrogen compounds present in the cheese without danger of coagulating any soluble proteids. The use of water at room temperatures is not, in our experience, equally effective in making a complete extraction of the water-soluble products. Under some conditions, as in the early stages of ripening cheese at low temperatures, small amounts of a body which is precipitated by heat in neutral solution are extracted by water. We are unable to say at present whether this body consists of acid salts of paracasein or of heterocaseose, which are practically insoluble in water, or whether it is some other compound. The temperature of 50° C. also has the advantage of arresting further peptic or tryptic action during the extraction. The use of acids in extracting cheese is to be avoided, since a small amount of acid will not only precipitate the soluble nuclein, but may form salts with paracasein, which are somewhat soluble in a slightly acid solution. The amount of dissolved paracasein salts under such circumstances

depends on the amount of acid used and the time of extraction.

4. *Determination of Total Water-Soluble Nitrogen.*

For the determination of the amount of total water-soluble nitrogen we take 50 cc. of the water extract, prepared as described above, equivalent to 2.5 grams of cheese, and treat it according to the Kjeldahl method for determining nitrogen.

5. *Determination of Nitrogen in the Form of Paranuclein (Pseudonuclein).*

To 100 cc. of the water extract, equivalent to 5 grams of cheese, we add 5 cc. of a 1 per cent solution of hydrochloric acid, and warm the mixture on the water-bath at 50° to 55° C., until complete separation takes place, as shown by a clear supernatant liquid. The precipitate is filtered, washed with water, and is then, with the filter-paper, treated by the Kjeldahl method to determine the amount of nitrogen. The amount found equals the nitrogen present in the form of paranuclein (pseudonuclein).

In our early work we used 2 or 3 cc. of a saturated solution of alum for this determination, for the reason that, in the separation of casein in milk, we had used this reagent successfully, but at the time we did not know the nature of the body we were precipitating from our water-solution of cheese. Later, when we had studied it and learned its character, we found, on comparing precipitations by the use of alum and by hydrochloric acid, that alum gave high results, undoubtedly precipitating some caseoses. In 27 comparative trials with water extracts of different cheeses, we found in the alum precipitate nitrogen varying from 0.2 to 0.337 per cent of the cheese, and averaging 0.269 per cent, while the nitrogen in the hydrochloric acid precipitate varied from 0.046 to 0.145 per cent of the cheese, and averaged 0.085 per cent. The nitrogen precipitated by alum in these 27 cases was from 2.1 to 5.5 times as much as that precipitated by hydrochloric acid, the average of all being 3.2. Since hydrochloric acid is known to precipitate paranuclein completely, we are

justified in assuming that the alum precipitates other com-
pounds, and this is confirmed by other work, showing that
when alum is used as the first precipitant, we get smaller
quantities of caseoses in the filtrate than we do when we use
hydrochloric acid as the precipitant of paranuclein. Alum
appears to resemble zinc sulphate as a precipitant of proteids.

Paranuclein (pseudonuclein) results from the breaking
down of casein or paracasein, and is always found in the
water extracts of ripening cheese, whether salted or unsalted.
It may, perhaps, be regarded more accurately as a residue,
and probably should not be counted as one of the products to
be used in measuring the extent of cheese-ripening. This is
undoubtedly the same body as Chittenden's dyspeptone,[1]
which he found as an insoluble residue in a pepsin-hydro-
chloric acid digestion of casein.

6. *Determination of Nitrogen in the Form of Proteids Coagulable by Heat in Neutral Solution.*

The filtrate from the preceding determination, 5, is made
neutral with dilute caustic potash, using phenolphthaleïn as
indicator. It is then heated at the temperature of boiling
water until any coagulum that forms settles completely, leav-
ing a clear, supernatant liquid. The precipitate is washed
with water and its nitrogen determined by the Kjeldahl
method. In our experience, such a precipitation rarely oc-
curs except in the case of cheese ripened near freezing-point.
The nature of this body we have not yet investigated.

7. *Determination of Nitrogen in the Form of Caseoses (Albumoses).*

The filtrate from the preceding determination, 6, is treated
with 1 cc. of 50 per cent sulphuric acid, saturated with pure
zinc sulphate, and then warmed to about 70° C., until the
caseoses separate completely and settle. The mixture is al-
lowed to cool and is then filtered. If filtered hot, there will
occur a further separation of caseoses in the filtrate on cool-
ing. The precipitate is washed with a saturated solution of
zinc sulphate made slightly acid with sulphuric acid. The

[1] Studies in Physiol. Chem., Yale Univ., **3**, 66 (1887-8).

nitrogen in the precipitate is determined by the Kjeldahl method.

For the determination of caseoses, the use of ammonium sulphate was exclusively employed, until Bömer[1] proposed the use of zinc sulphate, which possesses a distinct advantage in enabling one to determine nitrogen directly in the precipitate or filtrate. This method has been employed in the estimation of caseoses, also by the Wisconsin Agricultural Experiment Station. In the present state of our knowledge of this class of compounds, zinc sulphate must be regarded as the most available reagent for their quantitative separation.

8. *Determination of Nitrogen in the Form of Amido Acid Compounds.*

The amido acid compounds are determined in the filtrate from the precipitation of peptones, 9. For the removal of peptones, three reagents have been commonly used, (1) tannin and sodium chloride, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. After the removal of peptones the filtrate contains amido acid and ammonia compounds. After determining the amount of total nitrogen in this filtrate and then the amount of nitrogen present in the form of ammonia, as obtained in 10, page 167, we subtract the amount of ammonia nitrogen from the combined amount of amido acid and ammonia nitrogen, and thus obtain the amount of amido acid nitrogen. In the following section, 9, we describe the methods involved in removing peptones by the different reagents, and the efficiency of each reagent.

9. *Determination of Nitrogen in the Form of Peptones.*

(1) *By Tannin and Sodium Chloride.*—We place 100 cc. of our water extract of cheese in a 250 cc. graduated flask, add 1 gram of sodium chloride and a solution containing 12 per cent of tannin, until 1 drop added to the clear supernatant liquid gives no further precipitate. We then dilute to the 250 cc. mark, shake, filter through a dry filter, and determine the amount of nitrogen in 50 cc. of the filtrate by the Kjeldahl method. This gives us the amount of nitrogen in the form of amido

[1] Ztschr. anal. Chem., **5**, 562 (1895).

acid and ammonia compounds. The amount of nitrogen in the form of peptones is determined by difference, that is, by subtracting from the amount of total nitrogen in the water extract the combined sum of the amounts of nitrogen found in 5, 6, 7, 8, and 10.

The combination of tannin and salt has been settled upon by us as the most satisfactory for the separation of casein-derived peptones from amido acid compounds in milk and cheese analysis, when, as is commonly the case, we have large amounts of amido acid compounds relative to peptones. We have confirmed Schjerning's[1] results, showing that this reagent does not precipitate the monoamido acid compounds, such as leucine, tyrosine, aspartic acid, glutamic acid, and amidovaleric acid, nor does it precipitate histidine, arginine, lysine, cadaverine, putrescine, lysatine, or ammonia. In our work the tannin-salt solution has nearly as great a precipitating power as phosphotungstic acid, precipitating 93.3 per cent of the total nitrogen compounds present in a sample of fresh milk. In a study of ripened cheese, it precipitated the uncrystallizable end-products, caseoses and peptones, so completely that no further trouble was experienced in separating the crystallizable end-products.

It is well to record here the fact that when precipitation of peptones with tannin salt solution is attempted in a mineral acid solution, no precipitation occurs. It is only in neutral solution that more complete precipitation takes place.

The chief objection to the use of tannin-salt solution as a means of separating caseoses and peptones from amido acid compounds and ammonia is that it does not completely precipitate peptones. Hence, when we use the reagent for this separation, we commonly leave some peptones to be estimated as amido acid compounds, the amount of peptones thus being made smaller, and the amount of amido acid compounds larger, than the quantity actually present. Under our discussion of the use of phosphotungstic acid as a reagent for separating these classes of nitrogen compounds, we will give for comparison some results secured by each of the two reagents.

[1] Ztschr. anal. Chem., **39,** 545 (1900).

(2) *By Phosphotungstic Acid with Sulphuric Acid.*—In a 250 cc. graduated flask we place 100 cc. of the water extract of cheese, add 100 cc. of water and then 5 cc. of strong sulphuric acid. To this we add phosphotungstic acid of 30 per cent strength, until 1 drop gives no further precipitation in the clear supernatant liquid. We then dilute to the 250 cc. mark and filter through a dry filter. In 50 cc. or 100 cc. of this filtrate we determine the amount of nitrogen by the Kjeldahl method, and then the amount of peptones is obtained by difference.

Phosphotungstic acid has come into very general use in this country and in Europe as a means of separating peptones from amido acid compounds in work with cheese and milk. The work of Stutzer[1] and of Bondzynski[2] agrees in showing that phosphotungstic acid is a complete precipitant of casein, caseoses and peptones, while in their experience it does not precipitate the amido acid compounds or ammonia. Freudenreich and Jensen in all their work, even of recent date, have used this reagent in the cold as a means of separating peptones from amido acid compounds. Babcock, Russell, and Vivian, in this country, have used it, as well as tannin, designating the different precipitates as '' peptones by phosphotungstic acid'' and '' peptones by tannin.''

In the introductory portion of this paper, when mentioning different cleavage-products of casein, we included among them the hexone bases, *viz.*, arginine, histidine, and lysine, and, in addition, certain compounds resulting from their cleavage, such as putrescine and cadaverine, and also pyrrolidine-*a*-carbonic acid, all of which are precipitated by phosphotungstic acid. While not all these products have been separated from ripening cheese, it is probable that they will be sooner or later. We shall soon publish results of work done in this laboratory, showing in normal ripening cheese the presence of histidine, lysine, putrescine (derived from arginine),[3] and Siegfried's lysatine, which is also precipitable by phosphotungstic acid. The quantities of these bases that can be de-

[1] Ztschr. anal. Chem., **35**, 493 (1896).
[2] Landw. Jahrb. der Schweiz, (1894).
[3] A. Ellinger: Ber. d. chem. Ges., **31**, 3183 (1898).

rived from casein are not to be neglected, since, for example, in a hydrochloric-acid cleavage 15.4 per cent of the nitrogen of the products is split off in the hexone bases. Bondzynski has used phosphotungstic acid in hot solution with arginine and finds the precipitate soluble when hot, separating out on cooling, and this statement we can confirm, the solution, however, being complete only on boiling. In the case of lysine, histidine, and putrescine, the phosphotungstic acid precipitate fails to redissolve completely at the temperature of the water-bath or on boiling. This behavior renders worthless the use of phosphotungstic acid as a reagent for the separation of peptones from those amido acid compounds that are precipitated by it.

We have seen that tannin-salt solution fails to precipitate peptones completely and that phosphotungstic acid precipitates, in addition to peptones, some amido acid compounds. When, therefore, we use these two reagents in precipitating solutions that contain both peptones and amido acid compounds, as in the case of normal ripening cheese, we should expect to find the amount of nitrogen compounds left in the filtrate less with phosphotungstic acid than with tannin. This is found invariably to be the case. Vivian[1] has published some results obtained with nine different cheeses, which illustrate this point. We give his figures in the following table.

Table I.—Comparison of Phosphotungstic Acid and Tannin-Salt Solution in Precipitating the Nitrogen Compounds Contained in Water Extracts of Cheese.

No. of sample.	Percentage of nitrogen in cheese found in filtrates after precipitation by	
	Phosphotungstic acid.	Tannin-salt solution.
1	1.08	1.54
2	1.00	1.26
3	0.82	1.12
4	0.63	0.65
5	0.67	1.16
6	1.69	1.87
7	0.95	1.08
8	1.10	1.36
9	1.22	1.42
Average,	1.02	1.27

[1] Ann. Rept. Wis. Expt. Sta., **16**, 171 (1899).

In connection with the above results, nothing was stated in regard to the history of the cheeses used in the work. We have been able to study the action of phosphotungstic acid and tannin-salt solution in connection with samples of cheese that were under known well-controlled conditions, enabling us to know something of the general character of the proteolytic changes taking place. We placed 25 grams of cheese curd in each of several Erlenmeyer flasks, added 50 cc. of water, and sterilized the contents by heat. We then added 0.5 gram of concentrated lactic acid, in order to convert the paracasein into unsaturated paracasein lactate.[1] To some of the flasks thus prepared we added sterilized pepsin, and to others sterilized rennet extract. For this purpose the enzymes were prepared as follows : We dissolved 600 milligrams of Parke, Davis & Co.'s aseptic pepsin in 25 cc. of water, added 0.5 per cent of formalin (containing 40 per cent of formaldehyde), and let the solution stand until bacteriological examinations, made by Mr. H. A. Harding, showed the absence of living organisms. The mixture was then diluted to 100 cc. with water, and to each flask containing cheese we added 10 cc. of this sterilized pepsin solution. One thousand parts of the mixture in each flask thus contained one part of pepsin.

In preparing the sterilized solution of rennet, we diluted 5 cc. of Hansen's rennet extract to 25 cc. with water, added 0.5 per cent of formalin, proved the completeness of sterilization by bacteriological examinations, diluted to 100 cc., and added 10 cc. of this preparation to each flask containing cheese.

The flasks thus prepared were kept at 15°.5 C. The analytical results given below were obtained at the end of two and four weeks. In this work we had only the enzymes of pepsin and of rennet pepsin acting upon our proteid. Under these conditions, especially in the given length of time, we should not expect the formation of any considerable amount of amido acid compounds precipitable by phosphotungstic acid. The results obtained are given in the following table :

[1] N. Y. Agr. Expt. Sta., Bull. No. 214, p. 67 (1902).

Table II.—Comparison of Phosphotungstic Acid and Tannin-Salt Solution in Precipitating the Nitrogen Compounds Formed by Peptic Digestion of Cheese.

No. of sample.	Per cent of nitrogen in cheese found in filtrate after precipitation by	
	Phosphotungstic acid.	Tannin-salt solution.
1	0.10	0.45
2	0.10	0.44
3	0.150	0.645
4	0.175	0.685
5	0.10	0.48
6	0.08	0.46
7	0.16	0.73
8	0.16	0.70
Average,	0.128	0.574

In every case except one, the amount of nitrogen not precipitated by tannin-salt solution was more than four times the amount obtained by phosphotungstic acid. No ammonia was present in any case. In view of these widely differing results in relation to the amounts of amido acid compounds found, the questions may be asked, Which reagent more nearly represents the amount of amido compounds actually present ? Does the tannin-salt reagent fail to precipitate the peptones completely, thus allowing the unprecipitated peptones to be counted among the amido acid compounds ? Or does the amount of nitrogen in the filtrate in case of this reagent really represent amido acid compounds ? Does the phosphotungstic acid precipitate some of the amido compounds simultaneously with the peptones, thus cutting out a part of the amido acid compounds, and counting that part among the peptones ? Or is there in the cheese only the small amount of end-products indicated by the action of the phosphotungstic acid ?

While we did not by individual isolation determine to what extent amido compounds were present, we are justified in believing that such compounds were not yet present in the cheese in any appreciable degree ; and, hence, the figures obtained with phosphotungstic acid are much nearer the truth than those obtained by tannin-salt precipitation. We will state

our reasons for this belief. The amido compounds precipitated by phosphotungstic acid are known to be chiefly the diamido compounds, while the monoamido compounds are precipitated little, if at all. Hence, the compounds found in the filtrate of a phosphotungstic acid precipitation are mainly monoamido compounds. Now let us assume temporarily that the amounts of nitrogen in the tannin-salt filtrate, given in the table above, represent the total amido compounds, free from peptones. Then, since the monoamido compounds are represented by the amounts of nitrogen obtained in the phosphotungstic acid filtrate, the difference between the two sets of figures, that is, those obtained by tannin-salt solution and those obtained by phosphotungstic acid, represents the amount of diamido compounds. Taking the average of the results given in the table above, the nitrogen of the total amido compounds is 0.574 per cent of the cheese, while the nitrogen of the monoamido compounds is 0.128 per cent of the cheese, thus leaving the difference as the nitrogen of the diamido compounds, equivalent to 0.446 per cent of the cheese. According to these figures, the monoamido compounds constitute about 22 per cent of the entire amount of amido bodies, while the remainder, 78 per cent, represents largely diamido compounds. In this case the ratio of monoamido to diamido compounds is as 1 to 3.5. Keeping these data in mind, we will call attention to some work done by Hart[1] in studying the end-products of cleavage formed by the action of hydrochloric acid on casein. He found that the diamido compounds formed less than 20 per cent of the total amido compounds, so that the ratio of monoamido to diamido compounds was as 1 to 0.25 or less. In other words, the monoamido compounds were greatly in excess of the diamido compounds, or just the reverse of what we find to be the case in the results embodied in the table above, based on the assumption that the nitrogen in the tannin-salt filtrate represents the total amido compounds and nothing more. The most obvious and rational explanation of this discrepancy, observed in the ratio of monoamido to diamido compounds, is that it is wrong to assume

[1] Ztschr. physiol. Chem., **33**, 347 (1901).

that the tannin-salt filtrate contains only amido compounds and not any peptones. Withdrawing that assumption, then, and allowing that the nitrogen in the tannin-salt filtrate represents some peptones as well as the amido compounds, how can we tell in this particular case the true amount of amido compounds in the cheese? Unquestionably, the results with phosphotungstic acid more nearly represent the truth in regard to the amido compounds, because, under the conditions of the experiment, we should expect very small amounts of amido compounds, if any; and, in this particular case, the amounts are so small as practically to indicate the absence of amido bodies altogether. From this it may be seen that it is possible for the tannin-salt reagent to give results that are decidedly misleading.

(3) *By Bromine with Hydrochloric Acid.*—To the filtrate from the zinc sulphate precipitate in 7, we add 2 or 3 drops of strong hydrochloric acid, and then bromine until the liquid becomes saturated and there remains, after vigorous agitation, an undissolved globule of bromine amounting to 0.5 to 1 cc. This is allowed to stand over night. The precipitate is then filtered and washed with saturated bromine water. The nitrogen in the precipitate is then determined by the Kjeldahl method, and is called nitrogen in the form of peptones, the filtrate containing the amido acid compounds and ammonia.

The use of chlorine by Rideal and Stewart[1] in precipitating proteids suggested to Allen and Searle[2] the use of bromine. They reported that bromine quantitatively precipitates the products formed by the peptic digestion of egg-albumin, and they developed the method practically as given above. As applied to the separation of peptones from amido acid compounds in cheese and milk, the method gives varying results, depending upon the age of the cheese or milk used.

In the case of our water extracts made from cheese nine months to a year old, crystalline bodies in noticeable quantities are precipitated by bromine along with peptones, due

[1] Analyst, **22**, 226 (1897).
[2] *Ibid.*, **22**, 259 (1897).

probably to the presence of tyrosine, giving the solution a turbid appearance and rendering filtration difficult. Schjerning[1] has shown that tyrosine behaves in this manner with bromine water. This precipitate is partly retained on the filter-paper and is estimated as peptone.

Schjerning has shown also that bromine does not completely precipitate milk proteids and their derived caseoses and peptones. Of the whole proteid, he obtained only 76.7 per cent by bromine. In the case of milk, we have obtained results varying with the age of the milk. In perfectly fresh milk, when the amount of amido compounds must have been least, we obtained 91.3 per cent of the entire milk proteids by bromine precipitation. In another case of fresh milk we compared the precipitation of proteids by bromine and hydrochloric acid with that by tannin and sodium chloride, and by phosphotungstic acid solution and sulphuric acid, with the following results :

Precipitated by	Per cent of total nitrogen.
Phosphotungstic and sulphuric acids	93.8
Tannin and sodium chloride	93.3
Bromine and hydrochloric acid	91.5

There is also a possible source of error in connection with the use of bromine in precipitating peptones, when the filtrate from the bromine precipitate is used directly for the determination of amido acid compounds. We have found in the case of water extracts from cheese over one year old that there is an actual loss of nitrogen when bromine is allowed to stand in contact with the water extract. In the case of one cheese two years old, the cheese extract, consisting of caseoses, peptones, and amido acid compounds, contained nitrogen equivalent to 3.74 per cent of the cheese before adding bromine, while, after standing one hour in contact with bromine in hydrochloric acid solution, there remained only 1.52 per cent of nitrogen. In other words, there had disappeared 44.6 per cent of the nitrogen present before the addition of bromine. In cheese one year old we have found the loss varying from

[1] Ztschr. anal. Chem., **39,** 545 (1900).

:

nothing, in one case, to over 5 per cent in others. To show whether or not this loss came from the action of bromine on the caseoses or peptones, we removed the caseoses with zinc sulphate and, in another sample of cheese extract, we removed the caseoses and peptones with phosphotungstic acid, and the loss still occurred. By passing a current of air through the above extract in contact with bromine, and then through potassium hydroxide and through sulphuric acid, these reagents were found free from nitrogen compounds, indicating that the lost nitrogen disappeared in the form of free nitrogen, and not in the form of ammonia or nitrogen oxides. We cannot regard the method of determining the amount of peptones in cheese extracts by means of bromine as a reliable method, because, first, bromine precipitates small amounts of tyrosine and perhaps certain other similar compounds ; second, it is not a complete precipitant of caseoses and peptones ; and, third, its filtrate cannot be used for the determination of amido acid compounds, especially in old cheeses, owing to the decomposing effect of bromine upon such compounds, setting nitrogen free. In addition, bromine is a most disagreeable reagent to handle.

(4) *Comparative Value of Different Reagents Used in Separating Peptones and Amido Acid Compounds.*—We have now considered in some detail each of the three agents most commonly used in separating peptones from amido acid compounds, *viz.* : (1) Tannin-salt solution, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. Tannin and salt solution fails as a perfect reagent for the separation, because it does not completely precipitate peptones, which results in making the quantitative results for amido acid compounds too high, and may indicate the presence of considerable quantities of amido acid compounds even when they are practically absent. Phosphotungstic acid, on the other hand, completely precipitates peptones, but also precipitates some of the amido acid compounds that are present in cheese and milk, and the consequence is that the amount of amido acid compounds found is too low. Bromine is open to both

objections,—it fails to precipitate peptones completely, and at the same time does precipitate some of the amido acid compounds. While these two sources of error might tend to offset each other under certain conditions, we cannot depend upon such a method for reliable quantitative results.

In our judgment it is desirable, for best results, to use phosphotungstic acid to separate peptones and amido acid compounds, when the amount of the latter is relatively small as compared with peptones, or when they consist mostly of monoamido compounds. This condition occurs in the early stages of cheese ripening and persists longer in cheese cured at low temperatures. It occurs also in milk and cheese acted upon by pepsin enzymes, especially in the presence of chloroform.

Tannin-salt solution can be relied upon to give better results than phosphotungstic acid, when amido acid compounds are present in proportions that are relatively large compared with peptones, or when they consist largely of diamido compounds. The former condition prevails in normal cheese cured under usual conditions, especially after the first few weeks of curing.

10. *Determination of Nitrogen in the Form of Ammonia.*

We distil with magnesium oxide 100 cc. of the filtrate from the tannin-salt precipitation, passing the distillate into a standardized acid, and titrating in the usual way. In our early work the cheese mass itself, suspended in water, was used for distillation, giving slightly higher results than the method just described. The small increase is generally accounted for as coming from the proteids themselves present in the solution. Theoretically, it is true that when such bases as putrescine and cadaverine are present, they might distil with the ammonia. In one case where a large quantity of cheese was subjected directly to distillation with magnesium oxide and the distillate examined for these bases, none was found, the distillate containing only ammonia. The high boiling-points of cadaverine and putrescine, and the consequent difficulty of distilling them with steam probably accounts for their absence in the distillate.

In our early work on the determination of ammonia in milk
and cheese, we subjected to distillation with magnesium oxide
and with barium carbonate many different amido compounds,
in order to ascertain if any of these bodies, when pure, could
split off basic nitrogen. While some of the products used in
our work are not at all likely to be found in cheese or milk,
we include them with the others in the table given below.
The method was carried out as follows : We dissolved 1
gram of each amido body, or, if insoluble, suspended it in 50
cc. of water, and, for distillation, used 10 cc. of this mixture
diluted to 150 cc., adding magnesium oxide or barium car-
bonate and using ordinary atmospheric pressure.

*Table III.—Effect of Distilling Amido Bodies with Magnesium
Oxide and with Barium Carbonate.*

	Amount distilled with magnesium oxide.	Amount distilled with barium carbonate.
Acetamide	o	o
Allantoin	o	o
Arginine[1]	o	o
Aspartic acid	o	o
Creatine	o	o
Creatinine	o	o
Diphenylamine	o	o
Glutamic acid	o	o
Glycocoll	o	o
Histidine	o	o
Leucine	o	o
Lysine	o	o
Phenylenediamine	o	o
Trimethylamine	completely distilled	completely distilled
Tyrosine	o	o
Uric acid	o	o
Xanthine	o	o

We have also used the excellent Nencki apparatus, dis-
tilling under reduced pressure the filtrate from the tannin-salt
precipitation. In comparative trials we have obtained no
lower results than when we distil under ordinary atmospheric
pressure.

[1] Ztschr. physiol. Chem., **34,** 145 (1901).

11. *Determination of Nitrogen in the Form of Unsaturated Paracasein Lactate.*

The residue insoluble in water is treated with several portions of a 5 per cent solution of sodium chloride, the process being carried out as in preparing the water extract in 3, above. The nitrogen in an aliquot part of the 500 cc. of this salt extract is determined by the Kjeldahl method.

II. METHODS FOR THE SEPARATION AND ESTIMATION OF THE NITROGEN COMPOUNDS OF MILK AND THEIR PROTEOLYTIC PRODUCTS.

We will briefly describe the methods used for the separation and estimation of the nitrogen compounds of milk and their proteolytic products in order.

1. *Determination of Total Nitrogen in Milk.*

Weigh about 5 grams of milk and determine the nitrogen by the Kjeldahl method.

2. *Determination of Casein.*

To about 10 grams of milk add 90 cc. of water at 40° to 42° C., and then 1.5 cc. of 10 per cent acetic acid. Agitate and warm at the temperature given above until a flocculent precipitate separates, leaving a clear supernatant liquid. Filter, wash, and treat by the Kjeldahl method for estimating nitrogen.

In fresh milk, 2 or 3 cc. of a saturated solution of alum may be used in place of acetic acid, usually with little higher results. But when the milk-casein has been proteolyzed to any extent the use of alum is not permissible, since it precipitates caseoses in addition to casein.

The use of acetic or any other acid in precipitating casein in milk, whose casein has been digested in any degree, precipitates, in addition to casein, any paranuclein that is present. We have not yet succeeded in devising satisfactory methods for the separation of these two compounds.

3. *Determination of Nitrogen in the Form of Albumin and Syntonin.*

The filtrate from 2 is neutralized by caustic alkali, using phenolphthalein as indicator, and is then heated at the temperature of boiling water until the precipitate completely separates and settles. The precipitate is then filtered, washed, and treated by the Kjeldahl method.

4. *Determination of Nitrogen in the Form of Caseoses.*

The filtrate from 3 we heat to 70° C., add 1 cc. of 50 per cent sulphuric acid, and then pure zinc sulphate to saturation. Let stand at the temperature indicated until the caseoses completely separate and settle. Then cool the mixture, filter, wash with a saturated solution of zinc sulphate made slightly acid with sulphuric acid, and treat the precipitate by the Kjeldahl method.

5. *Determination of Nitrogen in the Form of Amido Acid Compounds.*

Treat about 50 grams of milk with a tannin-salt solution or with phosphotungstic acid according to directions given under 8, page 157.

6. *Determination of Nitrogen in the Form of Peptones.*

From the total nitrogen subtract that found in all forms other than that of peptones, as indicated under 9, page 157.

7. *Determination of Nitrogen in the Form of Ammonia.*

See under 10, page 167.

III. DETERMINATION OF CHLOROFORM.

When chloroform is used as an antiseptic in milk and cheese, it is very essential to know approximately the amount present in order that we may have proper control of the conditions. We have used the following method successfully : We place 5 grams of milk or cheese in a pressure-bottle with about 100 cc. of alcohol and 5 grams of caustic potash. The bottle is then heated in an autoclave for half an hour at 110° C. The resulting chloride is determined by titration as for chlorine in sodium chloride.

XLII.—AN APPARATUS FOR CONTINUOUS VACUUM DISTILLATION.[1]

By Charles F. Mabery.

The occasional contributions to methods for vacuum distillation seem to indicate that a method is still wanting that shall combine convenience and efficiency. It is quite true that the various attachments that have been suggested and that are described in dealers' catalogues fall short of efficiency in essential details. In the great amount of vacuum distillation carried on in this laboratory during the last fifteen years, probably much exceeding what has been done elsewhere in a single line of work, a durable apparatus has been gradually evolved in which this work can be carried on as expeditiously as distillations under ordinary pressures.

One of the most essential features is a regulator to maintain a constant tension, and the stop-cock G with lever attachment formerly described[2] and constantly in use is very satisfactory.

The chief features to be provided for in a convenient apparatus are the following :

1. Exclusion of air from hot oil in still during change of receiver.

2. Admission of distillates into still without interruption.

3. Admission of air into receiver before removal of each fraction.

4. Exhaustion of receiver for new fraction without connection with still.

The complete apparatus in the form used at present is shown in the figure on the next page.

The fractions are drawn into the still through the tube closed by the nipper tap A. The still is exhausted by the tube N connecting the tube O with the vacuum reservoir D. The reservoir C is exhausted by the tube H, which connects with the water-pump through the tube P. Air is let into the receiver C by means of the cock I, and kept from the still by

the cocks E and F. The tube with the stop-cocks E and F affords a convenient means for separating fractions without interruption, and without admission of air into the still. The tube M leads to the manometer. By means of a single efficient water-pump the entire apparatus may be kept under a tension of 12 mm. or less during continuous distillation. By means of common corks, the apparatus is readily set up and easily kept tight by the use of rubber lute.

The tubes H and N may be given less rigidity by putting them together in sections with connectors. Any water that may occasionally run back from the pump is readily drawn out if the pipe P extends to the bottom of the reservoir D.

The apparatus in this form is especially adapted for the separation of fractions with high boiling-points. For very high temperatures the still must be packed in asbestos. For more volatile distillates a condenser should be inserted between the still and tube O, best by passing the exit tube of the still through the condenser. Our distillation flasks are made with a high exit tube to give a long neck, which is filled with broken glass resting on a piece of glass rod with a head, as previously described. As is evident from the figure, this

apparatus may be readily set up from supplies always at hand in the laboratory, except the tube O, which any glass-blower can make.

Suggestions as to details have been made by various assistants, especially by Mr. O. J. Sieplein, instructor in chemistry, who prepared the drawing.

NEW OSMOTIC MEMBRANES PREPARED BY THE ELECTROLYTIC PROCESS.

[PRELIMINARY ANNOUNCEMENT.]

By H. N. Morse.

The electrolytic method[1] is well adapted to the deposition, upon or within porous walls, of nearly every kind of precipitate which can be formed from electrolytes in solution. It affords, therefore, a ready means of ascertaining which of these possess the character of semipermeable membranes.

In view of the reasonable prospect that some of the membranes discoverable in this way will be found to have certain advantages over copper ferrocyanide, especially for the investigation of the osmotic pressure of particular classes of compounds, the author and others in this laboratory have undertaken to test in a systematic manner a large number of electrolytically deposited substances.

It is already apparent, as was probably to be expected, that the number of compounds which are capable of exhibiting the semipermeable character is very large. Of the substances thus far tested, the following have been found to manifest osmotic activity to a promising degree : the ferrocyanides of zinc,[2] cadmium, manganese, and uranyl ; the phosphates of copper and uranyl ; and ferric and aluminium hydroxides.

Up to the present time we have concerned ourselves exclusively with the question whether the substances under examination are active or not, and consequently have tested the compounds mentioned above with open manometers only. We are, therefore, not yet prepared to give any opinion as to

---

[1] This JOURNAL, **26**, 80 ; **28**, 1.

[2] Tamman : Wied. Ann., **34**, 299 (1888).

Obituary.

how any one of them will behave under high pressure. But after having extended our search for semipermeable membranes as far as seems expedient, we shall proceed to subject those which offer the greatest promise of usefulness to a more careful study.

JOHNS HOPKINS UNIVERSITY,
Dec. 26, 1902.

OBITUARY.

JOHANNES WISLICENUS.

Professor Johannes Wislicenus, of the University of Leipzig, well known from his work in organic chemistry, especially that upon geometrical isomerism among organic compounds, died on the 5th of December, 1902. He was born in Klein-Eichstädt, near Querfurt, on the 24th of June, 1835, and was the oldest of a number of children. His father, Gustav Adolf Wislicenus, was a man of pronounced ability and marked independence in thought and action. On account of his connection with the *Burschenschaft*, in 1824, and while still a youth, the elder Wislicenus was sentenced to twelve years imprisonment, but was released in 1829. He then fitted himself for the ministry and was subsequently pastor of churches at Klein-Eichstädt and at Halle. He soon, however, attracted notice on account of the liberality of his utterances upon religious topics, and, in 1846, he was deprived of his pastorate because of his lack of accord with the authorities. He subsequently became pastor of a liberal church (*freie Gemeinde*) at Halle, but, in 1853, upon the appearance of his treatise entitled "Die Bibel im Lichte der Bildung unserer Zeit," he was again condemned to two years imprisonment. He succeeded, however, in escaping with his family and came to Boston, Mass., where he associated himself with men of corresponding liberality of views. He subsequently removed to Hoboken, N. J., where he started a school, but in 1856 he returned to Europe, making his home at Zürich.

The facts regarding the elder Wislicenus here outlined are significant as explaining how it came about that Johannes Wislicenus spent three years in the United States, and as showing the religious persecution which caused both father and son to separate themselves from church organizations as such. In accordance with the wishes of Professor Wislicenus, the recent funeral services were conducted in the chemical

lecture room of the University and, so far as can be judged from available reports, by his colleague, Professor Ostwald.

Wislicenus had, before coming to Boston, taken up the study of mathematics and the natural sciences at Halle, and had served as assistant in the chemical laboratory there. During his stay in Boston he became assistant to Professor Horsford, at Cambridge, and upon his return with his father to Hoboken he conducted, for nearly two years, a general analytical practice, having a laboratory at Hoboken and traveling about the country. He also lectured at the Mechanics' Institute in New York. It is interesting to note that at this time he, like his father, interested himself in public affairs and spoke eloquently in favor of abolition principles.

Upon his return to Europe he resumed his study of chemistry at Zürich and was afterward again assistant at Halle, but soon qualified as *Privat-docent* at the university at Zürich. About 1860 he was made professor at the university, and was transferred to the polytechnic school in 1870. In 1871 he was made director of the entire school. In 1872 he accepted a call to the university at Würzburg, and in 1885 was called to the University of Leipzig.

Professor Wislicenus devoted himself almost exclusively to research in the domain of organic chemistry. His contributions to chemical science are extensive, and from the beginning his published work deals largely with the development of theoretical conceptions concerning the character of organic compounds and their interactions. Among the first of these is a monograph entitled " *Theorie der gemischten Typen,*" published about 1859. He afterward took an active share in the development of the modern views regarding valence and of the relation of the atoms as individuals to the structure of organic compounds. His name will, however, undoubtedly be most generally identified with the development of the conceptions of geometric isomerism among organic compounds and the methods for the study of this phenomenon.

The theory propounded nearly simultaneously by Le Bel and van 't Hoff that the optical activity of organic compounds was connected directly with the presence in the compound of one or more asymmetric carbon atoms, while it drew attention to the significance of the geometrical arrangement of the atoms within the space dominated by the molecule, remained comparatively unfruitful until about 1887. Wislicenus then published his monograph, " *Ueber die räumliche Anordnung der Atome in organischen Molekülen und ihre Bestimmung in geometrisch-isomeren, ungesättigten Verbindungen,*" in which he developed the application of the principle of geometric isom-

erism, and offered it as an explanation of the existence of such isomers as fumaric and maleic acids, tiglic and angelic acids, and crotonic and isocrotonic acids, for which no previous explanation had been found. From that date Wislicenus and his pupils accumulated a large amount of material in support of the Le Bel and van 't Hoff theory and his own development of it. This cannot be outlined here, but it may be said that the value of his contributions to chemical science lies not only in the accumulation of facts which are recorded as the result of his researches and those of his students, but in the incentive which his work has afforded to others for thought and investigation. In this connection his demonstration of the extensive use which can be made of acetoacetic ether and its derivatives in organic syntheses also deserves special mention.

Of the personality of Professor Wislicenus one can speak only with enthusiasm. Of large frame, with a magnificent head (the beauty of which in his later years was emphasized by a mass of snow-white hair and a heavy white beard), with a countenance of unusual intellectuality and kindliness, and with a full, sonorous voice, he represented a splendid type of manhood. In his lectures he spoke without notes, with great ease, and in language which, without being in any degree florid, was so full of well-rounded sentences that the effect produced upon the listener was akin to that produced by a musician whose every tone is so certainly true as to cause only a feeling of contentment and keen pleasure in his auditors.

The frank and kindly countenance was an index of the nature behind it. He had a complete abhorrence of all display and of the use of official titles which have little or no real significance. He was a warm friend, as well as an inspiring teacher, to all his pupils, and to many of them the knowledge that the last few years of his life have brought much pain and suffering has already been a source of regret. The news of his death will intensify this sorrow, while it will also recall many pleasant memories of a man whom it is good to have known and been able to count as a friend, and to whom chemical science will ever owe a debt of gratitude.

H. P. T.

REVIEWS.

RESEARCHES ON CELLULOSE. 1895–1900. By CROSS and BEVAN. New York : Longmans, Green & Co. 1901.

'' This volume, which is intended as a supplement to the

work we published in 1895, gives a brief account of researches which have been subsequently published, as well as of certain of our own investigations, the results of which are now for the first time recorded.'' The authors refer to the book entitled '' Cellulose,'' which was reviewed in a former number of this JOURNAL.[1] The greater part of the present work is taken up with abstracts of the original articles, as the material is of too varied a nature to permit of a continuous or connected treatment. The authors point out the immense importance of these researches and show that the carbohydrate industry is of more importance than the coal-tar industry, and urge greater activity on the part of English chemists in this direction. The book is printed on standard printing paper, made according to the specifications of the Society of Arts Commission, appointed to study the quality of papers both in relation to their several applications, and more especially for documents of permanent value. J. E. G.

WATER SUPPLY (Considered Principally from a Sanitary Standpoint). By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute. Third edition,[2] rewritten. New York : John Wiley & Sons. 1902. 8vo. vi + 448 pp. 40 figures and 22 half-tone plates. Cloth, Price $4.00.

Chemists and all others having to deal with water supplies will cordially welcome this new and practically rewritten edition of Professor Mason's standard work on '' Water Supply.'' In the present edition of the book, which is the third, the treatment of the following subjects deserves especial mention : The mosquito-malarial theory and the experiments of Celli and Manson touching upon the transmission of malaria ; The relation between the growth and decay of algæ and the resulting odors observed in waters, particularly those of lakes and reservoirs ; The relation of goitre to drinking water, and Kocher's investigations thereupon ; and Alessi's experiments as to the production of artificial typhoid in animals. Under the head of filtration, the author discusses the workings of the new filtering plants at both Albany and Ashland, together with statistics illustrating the influence of such filtration upon the death-rates due to typhoid. Much new material has been added under the subject of mechanical filtration, including a discussion of the new iron coagulant. Space is given to the consideration of the merits of the rival systems of filtration, American and English, and to the question of properly choosing between them for municipal filtra-

[1] This JOURNAL, **17**, 622.
[2] The first edition of this book was reviewed by Prof. Mallet, of the University of Virginia in this JOURNAL, **18**, 625 (1896).

tion. Under the title Self-purification of Streams the recent investigations concerning the pollution of the Illinois river by the opening of the Chicago drainage-canal are given and commented upon. The question of the purification of water by freezing, and the important question of the contamination of ice supplies are both fully covered.

A point of particular importance is touched upon in showing the tendency of dissolved gases, such as oxygen and carbon dioxide, to attack iron at boiler temperature.

All the statistical tables are brought up to date and the book is provided with an excellent index. The chapters upon the Chemical and Bacteriological Examination of Water have been omitted from the present edition, for the reason that they have been published separately in book form for the more convenient use of students. W. R. O.

A MANUAL OF VOLUMETRIC ANALYSIS. Treating on the subjects of Indicators, Test-papers, Alkalimetry, Acidimetry, Analysis by Oxidation and Reduction, Iodometry, Assay Processes for Drugs with the Titrimetric Estimation of Alkaloids, Estimation of Phenol, Sugars, Tables of Atomic and Molecular Weights. By VIRGIL COBLENTZ, PH.D., PHARM.M., F.C.S., Professor of Chemistry in the New York College of Pharmacy. Philadelphia : P. Blakiston's Son & Co. 1901. Price, $1.25 net.

" This manual is intended to serve as a systematic introduction to the principles of volumetric analysis based on modern theories. Especial attention has been devoted to the theory of ionization and its application to indicators."

This work is especially designed for the student of pharmacy and medicine, and is written in such a clear, logical manner that these students can gain a good idea of the principles involved, even in the short period which they generally have at their disposal.

The value of this book is further enhanced by the introduction in each case of a detailed description of the methods of ca.culation and of practical examples. A general idea of the field covered in this work can be obtained from the title.

J. E. G.

AMERICAN

CHEMICAL JOURNAL

THE HYDROLYSIS OF ORGANIC PEROXIDES AND PERACIDS.

BY A. M. CLOVER AND G. F. RICHMOND.[1]

In cases of autoxidation, hydroperoxide has been frequently met with. Kingzett[2] and Löw[3] have shown that in the case of oxidized turpentine oil the active oxygen is not originally present in the form of hydroperoxide, and Engler and Weissburg[4] have further pointed out the fact that in all cases where hydroperoxide has been observed among the products of autoxidation its presence could be explained by assuming a secondary reaction of water with the original product. They look upon this change not as a direct oxidation process but as a hydrolytic one, *i. e.*, one brought about by the interaction of the substance in question with hydrogen and hydroxyl ions. They call attention to the fact that if benzoic peroxide be added to a solution of titanic acid in sulphuric acid, the latter, in time, takes on the yellow color produced by hydroperoxide, and they find that acetic peroxide gives this coloration almost immediately. They attribute these colorations to the formation of hydroperoxide.

[1] Parke, Davis & Co. Fellow in the University of Michigan.
[2] J. Chem Soc. (London), **12**, 511; **13**, 210.
[3] Chem. Centrbl., 1870, p. 821.
[4] Ber. d. chem. Ges., **31**, 3047.

Brodie,[1] however, makes the statement that with water the peroxides separate into free acid and oxygen.

Baeyer[2] has saponified benzoic peroxide with sodium ethylate, and acetic peroxide with sodium hydroxide. In the former case he isolated benzoperacid, and in the latter showed that the resulting product had acquired the properties of a per-acid. He also points out that benzoic and acetic benzoic per-oxides are substances without action upon solutions of potassium iodide or indigo, and without odor, and concludes that the acquisition of such properties by these substances is probably to be attributed to a hydrolytic change in which peracids are formed.

Wolffenstein[3] has found that the peroxides of acetone and mesityl oxide separate hydroperoxide on warming with dilute sulphuric acid, and Baeyer[4] has further observed that phthal-monoperacid gives rise to hydroperoxide on heating the solution.

Numerous authors have noted the formation of hydroperoxide by the action of alkalies upon peroxides.

Freer and Novy[5] have studied the action of water upon benzoic acetic peroxide, and have found that the active oxygen gradually goes into solution, while considerable quantities of benzoic peroxide are formed.

The most interesting and extensively investigated organic peroxides are those of the acids. These substances are to be considered as derivatives of hydroperoxide, and those which have been thoroughly investigated are found to belong to one of two classes :

1. Peroxides, in which both of the hydrogen atoms in a molecule of hydroperoxide are replaced by acid radicals.

2. Peracids, in which only one of the hydrogen atoms is so replaced.

With the object of discovering the exact nature of the changes which these bodies undergo with water, and of giving a general expression to our results, we have carefully in-

---

[1] Ann. Chem. (Liebig), Suppl., **3**, 211.
[2] Ber. d. chem. Ges., **33**, 1569.
[3] *Ibid.*, **28**, 2265.
[4] *Ibid.*, **34**, 762.
[5] This JOURNAL, **27**, 161

vestigated the behavior of several representative peroxides and peracids. Our work enables us to draw the following conclusions :

1. Acid peroxides are completely hydrolyzed by water into acid and peracid. The time taken to complete the change varies, of course, with the nature of the peroxide and with its solubility in water. A 5 per cent solution of acetic peroxide is completely changed in the course of forty-eight hours, while with butyric or crotonic peroxides the change is very much slower. With benzoic peroxide it is so slow as to be scarcely detected in the course of several days. This change is a complete one in all cases which we have investigated, that is, the reaction is not a reversible one :

$$\text{R.OO.R} + \text{H}_2\text{O} = \text{ROH} + \text{R.OO.H.}$$
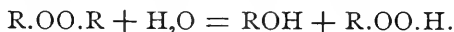
In case the peroxide is not homogeneous the hydrolysis may take place in two ways :

$$\text{R.OO.R'} + \text{H}_2\text{O} = \text{ROH} + \text{R'.OO.H,}$$

or

$$\text{R.OO.R'} + \text{H}_2\text{O} = \text{R.OO.H} + \text{R'OH.}$$
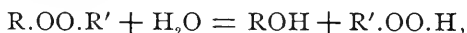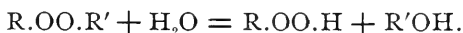
In the case of benzoic acetic peroxide the change was found to take place almost, if not altogether, completely in one way.

In the hydrolysis of peroxides of this class other products are met with, owing to a secondary reaction of the peracid first formed with the original peroxide. We have found that peracids in aqueous solution are extremely reactive toward substances capable of hydrolysis, such as acid chlorides, anhydrides, and peroxides :

$$\text{ROR} + \text{R'.OO.H} = \text{R.OO.R'} + \text{ROH} ;$$
$$\text{R.OO.R} + \text{R'.OO.H} = \text{R.OO.R'} + \text{R.OO.H.}$$
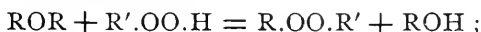
In all cases a peroxide is formed, together with an acid or a peracid. In case this peroxide is formed faster than it is hydrolyzed, it is evident that it will accumulate. In this way the less soluble and more slowly hydrolyzed homogeneous peroxide will be formed as a product of hydrolysis of a mixed peroxide, and the peracid which results from the reaction will be found in the solution.

2. Peracids are hydrolyzed into acid and hydroperoxide :

$$R.OO.H + H_2O = ROH + H.OO.H.$$
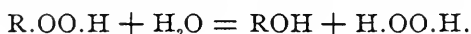
The change is a much slower one than the corresponding per-
oxide hydrolysis and, following the general law of hydrolytic
processes, takes place much more rapidly in acid solution.
This change is also a non-reversible one.

Acetic Peroxide.

Preparation.—Brodie[1] first prepared this substance by the
action of hydrated barium peroxide upon acetic anhydride,
the former being gradually added to a cooled ethereal solu-
tion of the latter. The yield which he obtained was very
poor. Nef[2] prepared it by the action of pure hydroperoxide
upon acetic anhydride, and Baeyer[3] makes the observation
that it is formed by adding acetic anhydride to an aqueous
solution of hydroperoxide. In working with considerable
quantities of this substance we have found the method of Nef
too laborious and that of Baeyer unsatisfactory as to yield.
We have again studied the action of barium dioxide upon
acetic anhydride, and have been surprised to find that under
proper conditions nearly a theoretical yield of the acetic per-
oxide may be obtained. Twenty-two and a half grams of
comparatively good barium dioxide (94 per cent) were cov-
ered with 30 cc. of water and shaken for a few minutes with
cooling. Twenty grams of acetic anhydride were added to
100 cc. of ether and cooled to 0°. The suspension of barium
dioxide was then gradually added, with shaking, during the
course of five minutes. The mixture was kept cooled to 0°
and shaken for about fifteen minutes, when the dioxide had
about disappeared. The ethereal layer was then removed by
decantation, dried for several hours over calcium chloride,
and the solvent then removed in a vacuum. The peroxide
begins to crystallize from the cold, concentrated solution, and
finally remains as a pure crystalline residue. It may be re-
crystallized from ligroin by cooling, in a freezing-mixture, a

[1] *Loc. cit.*
[2] Ann. Chem. (Liebig), **298**, 287.
[3] Ber. d. chem. Ges., **33**, 1569.

solution saturated at room temperature. Owing to the danger of spattering during the removal of the last portion of ether, it is advisable, on account of the extreme explosiveness of the substance, to dissolve the concentrated ethereal solution in ligroin and allow the peroxide to crystallize in a freezing-mixture. The yield was 8.8 grams. As the peroxide is probably formed according to the equation

$$2(CH_3CO)_2O + BaO_2 = Ba(C_2H_3O_2)_2 + C_4H_6O_4,$$
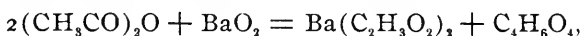
this amount represents 76 per cent of the total possible yield. Almost as good a yield may be obtained by using the cheaper and less pure barium dioxide, although in this case it is better to use more than the calculated amount, owing to the slow solubility of portions of the commercial article. If the solution be kept well cooled the yield is not greatly decreased by using excess of the dioxide. The pure peroxide liberates the theoretical amount of iodine from a solution of potassium iodide (best in 20 per cent acetic acid).

If the peroxide is dissolved in excess of $N/10$ potassium hydroxide and the solution heated on a water-bath for ten minutes, on titrating the excess of hydroxide the amount used will be found to correspond to 2 molecules for every molecule of peroxide.

The pure peroxide, shaken with water at $25°$ for five minutes, yielded a 0.935 normal solution of active oxygen. When the shaking was continued for ten minutes a 0.950 normal solution was obtained. At this rate of hydrolysis the real solubility may be placed at 0.920 normal, or 54.2 grams per liter.

As previously stated, this substance, like all acid peroxides having an appreciable solubility in water, liberates iodine from a solution of potassium iodide. The action of these substances in neutral or slightly acidulated solution is very slow, but is greatly increased in rapidity in more strongly acid solution. In this case, however, it is necessary to make a correction for the amount of iodine liberated from a blank solution under the same conditions. It is generally best to use acetic acid to acidulate with, as the solubility of the peroxides is thereby greatly increased.

If potassium iodide is added to a slightly acidulated, freshly prepared solution of acetic peroxide, there is no immediate liberation of iodine. On standing, however, the latter appears in the solution in gradually increasing concentration and the reaction is complete in three or four hours. If, however, the solution of peroxide is allowed to stand twenty-four hours before the addition of potassium iodide, its behavior is markedly different. In this case the liberation of nearly the entire amount of iodine takes place immediately. As will be shown later, the change which has produced this difference in behavior requires at least twenty-four hours to complete itself. As already noted, however, the liberation of iodine is complete in three or four hours in a non-hydrolyzed solution. This indicates that either a condition of equilibrium exists between the factors of the reaction, permitting the reaction to go to completion much more quickly by the removal of one of the products, or that the unchanged peroxide is itself an oxidizing agent. However, from a saturated solution of acetic peroxide which had stood a week, it was impossible to extract any of the unchanged substance by means of ligroin. The peroxide is more soluble in ligroin than in water. A small amount of active oxygen is taken up by the ligroin, but the former oxidizes potassium iodide immediately, and is therefore due to acetperacid. As the presence of small quantities of unchanged peroxide would be indicated by a further slow liberation of iodine, it may be concluded that the change is a complete one. From this and the similar behavior of other peroxides, it is to be assumed that they are themselves oxidizing agents.

This gradual change which a solution of peroxide undergoes may be followed in a rough way by noting, from time to time, the amount of iodine liberated immediately, the iodine being estimated by means of a $N/10$ solution of sodium thiosulphate. Of a freshly prepared solution, 5 cc. required a total of 20.2 cc. $N/10$ thiosulphate: after four hours the immediate liberation of iodine required an average of 9.7 cc.: at the end of eight hours, 14.6 cc. : after twenty-two hours, 19.3 cc. The solution stood at a temperature of 20°. The titration was

performed as quickly as possible after adding the potassium iodide, but even then the values obtained are not to be considered absolute, owing to the oxidizing action of the unchanged peroxide. The numbers indicate the general course of the change, however. A similar experiment with the analogously constituted propionic peroxide shows the progress of the change much more exactly.

Cryoscopic Determination.—0.655 gram acetic peroxide was dissolved in 25.703 grams water in an ordinary Beckmann apparatus. A lowering of $0°.444$ was produced.

Molecular Weight.

Calculated.	Found.
118	109

The solution was then allowed to stand at $20°$ and additional readings of the freezing-point were taken from time to time:

After	8 hours,	additional	lowering		$0°.223$
"	20 "	"	"		$0°.338$
"	24 "	"	"		$0°.343$
"	32 "	"	"		$0°.363$
"	44 "	"	"		$0°.380$
"	50 "	"	"		$0°.377$

Some little time was spent in dissolving the substance and getting conditions for the first reading, so that the latter is a little large, accounting for the low molecular weight found. At the end of two days there was little change in the freezing-point on further standing. The total depression of the freezing-point is $0°.821$. The calculated depression caused by a hydrolysis of 1 molecule of peroxide into 2 molecules is $0°.820$. It might not be expected that these numbers should agree quite so well, as it will be seen later that further changes take place in the solution. The experiment is in good agreement with the one in which the immediate liberation of iodine was estimated from time to time, and clearly demonstrates that the primary change is one in which 2 molecules are produced from one of the peroxide. As it will be shown further on

that one of these substances is acetperacid, the change may be expressed as follows :

$$CH_3CO.OO.COCH_3 + H_2O = CH_3CO.OO.H + CH_3COOH.$$
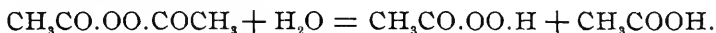
The Formation of Hydroperoxide.—If a saturated solution of acetic peroxide be subjected to the tests for hydroperoxide, only negative results are obtained, *i. e.*, chromic acid is not oxidized to perchromic acid, and a solution of titanic acid in dilute sulphuric acid is not colored. The latter solution, however, soon becomes yellow on standing, the more quickly, the more sulphuric acid is present, other conditions being the same. The rapid formation of hydroperoxide in this case is to be attributed to the hydrolytic influence of the sulphuric acid. In numerous cases in the literature, peroxides are described as responding to this test. It is highly probable that all such cases are due to the hydrolytic development of hydroperoxide due to the use of too strong sulphuric acid in preparing the titanic solution. None of the peroxides which we have examined respond to this test except on standing. On the other hand, the delicacy of the perchromic acid test for hydroperoxide is greatly decreased by the use of mineral acid, and for this reason it is more reliable, although not so delicate. It is easy to detect 1 part of hydroperoxide in 100,000 parts of water by covering the solution with ether, cooling, adding a grain of potassium bichromate, and then very dilute sulphuric acid drop by drop until the maximum coloration is produced. After the solution of acetic peroxide has stood for two hours, there are evidences of the formation of hydroperoxide by a slight immediate coloration with titanic acid. At the end of three hours a decided test is obtained with chromic acid. The first change, *i. e.*, the hydrolysis of acetic peroxide, has been shown to be practically complete in about two days. At the end of this time 93 per cent of the active oxygen in the solution causes immediate liberation of iodine. As it has already been shown that the solution at this point contains practically no acetic peroxide, this remaining active oxygen is to be attributed to hydroperoxide, which, like the acetic peroxide, liberates iodine very slowly in dilute acetic acid solution. The amount of hydroperoxide continues to increase on

standing, until at the end of a month nearly the entire active oxygen content of the solution is present in this form. It is evident, then, that the hydroperoxide results from the hydrolysis of the acetperacid,

$$CH_3CO.OO.H + H_2O = CH_3COOH + H.OO.H.$$
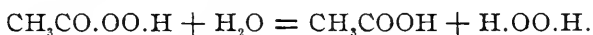
The following table shows the stability of a solution of acetperacid and the rate at which it is hydrolyzed into hydroperoxide. The numbers in the first column indicate the immediate liberation of iodine by 5 cc. of the solution, estimated as quickly as possible by a solution of N/10 thiosulphate; they represent acetperacid. The numbers in the second column indicate the total active oxygen in 5 cc. of the solution, due to acetperacid and hydroperoxide. In the third column are placed the differences between the total and immediate iodine representing hydroperoxide. Experiments with benzoperacid and hydroperoxide showed that, in dilute acetic acid, the two substances may be estimated in the presence of each other by this method :

Time in days.	Cc. thiosulphate. Immediate.	Cc. thiosulphate. Total.	Difference.
0	0.0	40.2	
2	37.3	40.0	2.7
3	35.1	39.3	4.2
4	32.0	37.5	5.5
5	29.0	36.7	7.7
9	24.7	35.5	10.8
15	18.2	34.3	16.1
22	11.8	31.4	19.6
30	5.4	28.0	22.6
34	3.4	26.5	23.1

Further Evidence of the Presence of Acetperacid.—From the behavior of the hydrolyzed solution toward potassium iodide, and by comparison with the similar behavior of the benzoperacid of Baeyer, it has been assumed that acetperacid was one of the products of hydrolysis. The following experiments conclusively decide this point :

Action of Acetic Anhydride.—An aqueous solution of acetic peroxide was allowed to stand twenty-four hours. It was then

extracted several times with ligroin, by which means small quantities of unchanged peroxide were removed, the hydrolyzed product being much more soluble in water and less soluble in ligroin than the peroxide. Two cc. of the solution then liberated iodine, requiring 14.2 cc. N/10 thiosulphate immediately and 0.8 cc. additional, due to hydroperoxide and unchanged acetic peroxide. Fifty-one cc. of this solution, representing 2.1 grams of acetic peroxide originally, were placed in a flask, cooled to 15°, and 4 grams of acetic anhydride added and dissolved by shaking. The solution was kept cooled to 15°. One cc. was removed at intervals (5 cc. in all), and the "immediate" titer was found to gradually decrease from its original value of 6.4 to 1.2 in about one-half hour, the total active oxygen content of the solution remaining the same (decreased slightly by the dilution with acetic anhydride). After this time it began to slowly increase again. After two hours it was extracted several times with ligroin. On evaporating the solvent and cooling, acetic peroxide crystallized out. 0.0764 gram analyzed for active oxygen required 12.7 cc. N/10 thiosulphate; calculated 12.9 cc. The amount of peroxide removed by extracting four times with 0.5 volume of ligroin was 0.7 gram, and an additional amount remained in the solution.

It will be recalled that before the addition of acetic anhydride the solution had been thoroughly extracted with ligroin, and only a very small amount of peroxide was obtained. Further, that the amount of hydroperoxide in the solution would account for the formation of only a trace of acetic peroxide. The following reaction, therefore, took place :

$$CH_3CO.OO.H + (CH_3CO)_2O =$$
$$CH_3CO.OO.COCH_3 + CH_3COOH.$$
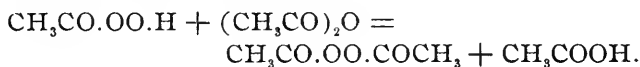
Action of Benzoyl Chloride.—Twenty cc. of an aqueous solution of acetic peroxide (1 cc. required 6 cc. N/10 thiosulphate) stood twenty-four hours. To the solution were added 2 grams of benzoyl chloride and an excess of sodium acetate. The mixture was shaken in a flask at 25° for ten hours, in which time the product had solidified. The solid product was dissolved

in ether and shaken out with a solution of sodium carbonate.
On evaporation of the ether a crystalline residue remained
which still retained the odor of benzoyl chloride, and was al-
lowed to lie exposed to the air until this had disappeared.
The residue consisted of a mixture of benzoic and benzoic
acetic peroxides, the difference in their solubility in ligroin
permitting of a separation. The latter substance separated
from the mother-liquor with difficulty, owing to the presence
of an oily impurity. After crystallizing several times, the
melting-point could not be raised beyond 36° (Baeyer, 38° to
39°). At this point there was not enough of the substance
left for analysis, but there is little doubt in our minds as to
its identity. The original residue consisted of about 25 per
cent of the benzoic acetic peroxide, estimated in dilute acetic
acid with potassium iodide and thiosulphate. The benzoic per-
oxide does not liberate iodine in dilute acetic acid. The ben-
zoic acetic peroxide was probably formed according to the fol-
lowing equation : ·

$$C_6H_5COCl + CH_3CO.OO.H = C_6H_5CO.OO.OCCH_3 + HCl.$$
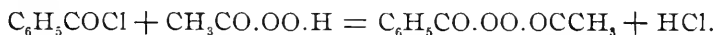
The formation of benzoic peroxide here, in such large quanti-
ties, is noteworthy and interesting. We are unable at pres-
ent to explain the process by which it is formed.

Acetperacid.—The isolation of this substance from an aque-
ous solution containing acetic acid presents great difficulties,
and we have not been successful in our attempts to do this.
As the chief interest in this substance lies in its oxidizing
properties, and as the solution as formed is quite well adapted
for its use in this respect, there is no special need for its iso-
lation. A few of the striking characteristics of the solution
are as follows : Indigo is bleached slowly, more rapidly with
the addition of dilute sulphuric acid. A weak solution of lit-
mus is not decolorized by a large excess of the oxidizing
agent in twelve hours. Chlorine is liberated from a dilute
solution of hydrochloric acid. A drop of potassium perman-
ganate is unaffected in a large excess of the solution weakly
acidulated with sulphuric acid. In strong acid solution
(1 : 5) it is soon decolorized, owing to its rapid hydrolysis into

hydroperoxide. If a grain of manganous acetate be added to an excess of the solution, a red coloration is produced which is somewhat obscured by the formation of manganese dioxide. If dilute sulphuric acid be previously added, the solution assumes the characteristic color of permanganic acid, and no manganese dioxide is formed unless considerable of the manganous salt is added. In strong sulphuric acid solution (1 : 5) the formation of permanganic acid is prevented. If potassium permanganate be added drop by drop to a solution containing both acetperacid and hydroperoxide, weakly acidulated with sulphuric acid, it is quickly decolorized until the hydroperoxide is destroyed. At this point the manganous salt begins to be reoxidized to permanganic acid, and the solution is soon deeply colored.

An attempt to estimate a known amount of hydroperoxide in the presence of a solution of acetic peroxide, which had stood for two hours, gave a result a little low, as might be expected, for, in the time required to make the titration, a small amount of the manganous salt formed by oxidation of hydroperoxide is reoxidized by the peracid to permanganic acid, thus decreasing the required amount of the latter.

The solution of acetperacid does not oxidize alcohol, which is shown by the fact that the amount of peracid in a solution to which alcohol had been added had not decreased on standing twenty-four hours. The same result was obtained by adding crotonic acid to a solution.

The solution gives no precipitate on addition of the acetates of silver, lead, mercury, or copper. With silver oxide and lead monoxide a rapid evolution of oxygen occurs. A solution of basic lead acetate shows the same behavior. Manganese dioxide shows no catalytic action but is oxidized to permanganic acid.

As the simplest representative of the organic peracids, it is quite probable that this substance will be found suitable for oxidizing purposes in certain cases, as has already been the case with the similarly constituted sulphuric peracid (Caro's reagent).[1] Its suitability for such purposes lies in the follow-

[1] Ber. d. chem. Ges., **32**, 1676, 3625.

ing facts : (1) It is easily prepared ; (2) a very concentrated solution may be made by continued hydrolysis of an excess of the peroxide ; (3) it is an organic oxidizing agent and the re-duction-product is unobjectionable.

As has already been observed, the acetic peroxide when caused to explode does so with great violence. During our work with this substance we have never observed an explo-sion except when it was heated or subjected to unnecessary friction. To prepare the substance pure, it is not necessary to handle it as the crystallization may be brought about in a flask, the mother-liquor removed by decantation, and the crys-tals washed and dried in a vacuum without removing them from the flask. We have employed this method repeatedly with-out accident. In cases where the presence of ether is unob-jectionable, the solution of acetperacid may be made by dis-solving in water the concentrated ethereal solution of the crude product.

Propionic Peroxide.

Preparation.—The method employed in making acetic per-oxide was used also in this case. Eight and a half grams of propionic anhydride were dissolved in 100 cc. of ether and cooled to 15°. Six grams of 95 per cent barium peroxide were suspended in 40 cc. of water, cooled to 15°, and added to the ethereal solution. On shaking for fifteen minutes the barium peroxide was dissolved. The maximum amount of propionic peroxide was not present in the solution until a total of 7.5 grams of barium peroxide had been added. Until this point was reached the solution still contained unchanged anhy-dride (found by comparing the amount of $N/10$ potassium hydroxide required by 1 cc. of solution with amount of $N/10$ thiosulphate required.) At the point of maximum yield the anhydride had disappeared, and the addition of more barium peroxide decreased the amount of propionic peroxide. The necessity for using an excess of barium peroxide is thus found, and that the yield of propionic peroxide (4 grams) does not equal the theoretical is also accounted for. The reaction, therefore, takes place according to the following equation :

$$2C_6H_{10}O_3 + BaO_2 = C_6H_{10}O_4 + BaC_6H_{10}O_4.$$

The ethereal solution was dried over calcium chloride, the ether evaporated in a vacuum, and the last traces completely removed by means of a current of dry air at 35° in a vacuum. The resulting product was analyzed as follows: The active oxygen was estimated by dissolving in 80 per cent acetic acid containing potassium iodide, and allowing to stand for one-half hour for complete liberation of the iodine. It was then diluted and the latter estimated by N/10 thiosulphate. A blank experiment was then made under the same conditions and the correction applied.

As a substitute for the difficult elementary analysis, the amount of potassium hydroxide required to convert a known amount into potassium propionate was determined. This method has already been spoken of under acetic peroxide. The substance was dissolved in an excess of N/10 potassium hydroxide, heated for ten minutes on a water-bath, and the excess of potassium hydroxide then determined by titration.

The residue of propionic peroxide, on removal of the ether, gave active oxygen and acid values both a little high. This could be accounted for only by assuming the presence of a small amount of acetic peroxide. This was confirmed by repeatedly shaking the product with small portions of water. The first washings contained much more active oxygen than the latter, the content of which soon became constant, representing the solubility of the pure propionic peroxide. Ten cc. required 10.9 cc. N/10 thiosulphate.

The saturated solution is therefore 0.109 normal and contains 15.9 grams per liter.

The washed product was again taken up with ether and dried. On complete removal of the solvent it gave analytical results showing that it was pure propionic peroxide:

0.1595 gram required 21.7 cc. N/10 thiosulphate; calculated 21.85 cc.

0.1395 gram required 19.0 cc. N/10 potassium hydroxide; calculated 19.1 cc.

The presence of a more highly oxidized form was at first suspected in the crude product. This is made impossible by

the fact that the potassium hydroxide and thiosulphate values, while both high, were exactly the same. The acetic peroxide was probably formed from acetic anhydride present as an impurity in the propionic anhydride employed.

The pure propionic peroxide is miscible with all the ordinary solvents. When heated to 80° a slow effervescence sets in, which continues until the decomposition is complete. Hydrocarbons and carbon dioxide are evolved, and the residue is a gum which dissolves completely in sodium carbonate and is again precipitated on acidifying. When subjected suddenly to a high temperature the peroxide explodes, but without the violence and detonation of acetic peroxide. At —20° it could not be induced to solidify. Owing to its instability, no attempt was made to distil it.

Hydrolysis.—In the case of acetic peroxide a rough idea of the course of its hydrolysis was obtained by determining the immediate liberation of iodine from time to time. In the case of propionic peroxide the progress of the reaction is shown quite nicely by this method. In dilute acetic acid the unhydrolyzed peroxide affects potassium iodide very slowly, so that by working quickly it is possible to estimate the amount of peracid in a solution accompanied by peroxide, without much error due to the latter.

The following table shows the behavior of a solution of propionic peroxide at a temperature of 20°. Five cc. of the solution required a total of 10.8 cc. N/20 thiosulphate. The numbers under "immediate iodine" represent the amount of thiosulphate required by 5 cc. of the solution from time to time. The relative values of the reaction-constant,

$$\left(K = \frac{1}{t} \log \frac{a}{a-x} \right),$$

have been calculated, assuming the reaction to be of the first order. In the first three determinations there is a remarkably good agreement in this value, as an error of 0.1 cc. in the titration numbers is sufficient to account for the variation. The lowness of the fourth value is probably due to the forma-

tion of hydroperoxide in the more concentrated solution of peracid.

Time in hours.	Immediate iodine. cc.	Reaction-constant.
3.0	3.0	471
6.5	5.4	463
11.5	7.6	459
23.0	9.8	449

The reaction is to be expressed as follows :

$$C_2H_5CO.OO.COC_2H_5 + H_2O = C_2H_5CO.OO.H + C_2H_5COOH.$$
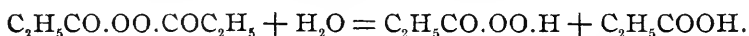
After twenty-four hours hydroperoxide may be detected in the solution.   In its chemical behavior propionic peracid is not to be distinguished from acetic peracid.

Crotonic Peroxide.

Crotonic Anhydride.—The general method proposed by Autenrieth[1] was employed with very satisfactory results. One hundred grams crotonic acid were boiled with 350 grams acetic anhydride for twenty-four hours, with reflux condenser. The acetic acid and excess of anhydride were then distilled off under diminished pressure.   The residue was taken up with ether and shaken out with the requisite amount of sodium carbonate for removal of unchanged acid.   It was then dried over calcium chloride and, after distilling off the solvent, was fractionated under diminished pressure.   About 60 grams of practically pure anhydride, boiling within 4° to 5°, were finally obtained.   The amount of mixed anhydride formed was small.   The highly purified crotonic anhydride boils at 128° to 130°, under 19 mm., with slight decomposition.   Its specific gravity at 29°, compared with water at the same temperature, is 1.0338.   It does not solidify at —15°.

Analysis : 0.1734 gram substance gave 0.3956 gram CO_2 and 0.1019 gram H_2O.

	Calculated for $C_8H_{10}O_3$.	Found.
C	62.34	62.21
H	6.49	6.53

[1] Ber. d. chem. Ges., **34**, 168.

0.1000 gram required 26.0 cc. N/20 potassium hydroxide to neutralize ; calculated 26 cc.

Preparation of Peroxide.—Seven and eight-tenths grams anhydride were dissolved in 100 cc. ligroin and added to 3.4 grams of hydroperoxide in 8 per cent solution. This mixture was cooled to 15°, and a saturated solution of barium hydroxide added in portions of 10 cc., shaking after each addition until the barium dioxide had disappeared. The mixture was kept cooled to 15°, and the course of the reaction was followed by estimation of the active oxygen content of 1 cc. of the solution from time to time. The latter showed a maximum value after the addition of 100 cc. (3.14 grams) of barium hydroxide. There was present in the solution at this point active oxygen to account for 3.9 grams of crotonic peroxide. On removing the ligroin solution and partially evaporating the solvent, the peroxide separates as crystals on cooling. Only about 2 grams of these crystals were obtained, the remaining product separating as an oil. This oil is probably an oxidation-product of the unsaturated crotonic anhydride in alkaline solution, for we have observed that hydroperoxide and peracids are much more powerful oxidizers in the presence of alkalies than in neutral or acid solution. The crystals which separated from the ligroin solution were practically pure. The pure substance consists of needles and irregularly shaped plates, and melts at 41°. It is odorless and explodes gently on heating. It does not decompose on long standing. It is soluble in all of the ordinary solvents.

The active oxygen was determined by dissolving in 10 per cent acetic acid and adding a solution of potassium iodide acidulated with dilute sulphuric acid. A blank experiment was made and the correction applied.

0.1182 gram substance required 13.8 cc. N/10 thiosulphate ; calculated 13.9 cc.

0.1249 gram treated with excess of N/10 potassium hydroxide required 30.7 cc. to neutralize ; calculated 29.4 cc.

This method of analysis is evidently not applicable in the case of an unsaturated peroxide. The elementary analysis was therefore made.

0.1328 gram substance gave 0.2737 gram CO_2 and 0.0705 gram H_2O.

	Calculated for $C_8H_{10}O_4$.	Found.
C	56.47	56.20
H	5.88	5.81

Hydrolysis.—This substance was selected on account of its being crystalline, with the intention of isolating the peracid formed. The slowness with which it hydrolyzes, however, renders it unsuitable for such study.

An excess of peroxide was added to water contained in a glass-stoppered flask and shaken at 25° for several days. The progress of the hydrolysis was ascertained by removing 25 cc. of the solution at intervals and determining the immediate liberation of iodine. The difference between immediate iodine and total iodine is seen to be the same in each case, representing the solubility of the unchanged peroxide, which remains constant. There is also seen to be a regular increase in the amount of peracid. The latter, therefore, appears to have no oxidizing action on the unsaturated carbon atoms.

Time in days.	Immediate iodine. Cc. N/10 thiosulphate.	Total iodine. Cc. N/10 thiosulphate.
2	1.35	4.1
4	2.7	5.5
8	5.2	7.9

A portion of the solution removed, after standing for one month, had lost only one-fourth of its active oxygen, which was then present almost entirely as peracid. At this time hydroperoxide could just be detected by means of the chromic acid test.

Another completely hydrolyzed solution of 0.3 gram peroxide in 50 cc. water was extracted with ligroin, thereby removing only a trace of peracid. On extracting twice with ether the peracid was completely removed, together with crotonic acid. On evaporating the ether a crystalline residue remained, which possessed the characteristic peracid odor.

Benzoic Acetic Peroxide.

The substance dissolved in dilute acetic acid liberates the

theoretical amount of iodine from potassium iodide. Its solubility in water at 25° amounts to 0.639 gram per liter.[1] This solution, on standing, suffers not only a change to peracid, as noted by change in the amount of iodine liberated immediately, but soon becomes turbid, owing to the separation of the insoluble benzoic peroxide. By adding an excess of the peroxide to water and shaking the mixture to keep the solution saturated, the benzoic peroxide gradually accumulates, while the soluble products remain in the solution. In this way a more concentrated solution of the latter is obtained, suitable for study.

Four grams of the peroxide were added to 250 cc. water and shaken at 25°. At intervals, given in the table below, a portion of the solution was filtered through glass wool, 10 cc. of the filtered solution removed, and its immediate and total liberation of iodine estimated with N/10 thiosulphate. After forty-two hours the presence of hydroperoxide was plainly shown by the chromic acid test. This accounts for the gradual increase in the amount of " additional iodine," which is made up of unchanged peroxide and hydroperoxide. The numbers in the column under " immediate iodine" give a general idea of the rate of formation of peracid. As this experiment was continued through a considerable space of time and peracids in solution are unstable, they represent less than the total amount of peracid formed.

The rate of hydrolysis, as represented by the rate at which the solution takes on active oxygen, is found to increase slowly during the course of the experiment, probably owing to the increased solubility of the peroxide and to the catalytic action of the acid formed.

Time in hours.	Immediate iodine.	Additional iodine.
21	3.8	0.8
42	8.0	0.9
52.5	10.3	1.0
73.5	14.3	1.3

The following experiments were performed with accurately weighed amounts of pure peroxide :

[1] Freer and Novy : *Loc. cit.*

1. 0.5180 gram was added to 50 cc. water and shaken in a sealed flask at 25° until the change was complete. As previously mentioned, a solution of benzoic acetic peroxide becomes decidedly turbid on standing, and this fact made it possible to ascertain the completeness of the reaction. After four days the flask was opened, the residue carefully filtered and washed, the washings being added to the filtrate. The residue consisted of 0.1726 gram pure benzoic peroxide (m. p. 107°.5). (As the filtration was made through glass wool the benzoic peroxide was not conveniently determined by estimating the active oxygen. Experiments with pure benzoic peroxide showed the following method to be accurate : The peroxide is dissolved in 80 per cent acetic acid containing potassium iodide and allowed to stand one hour, when the solution is diluted and the iodine estimated. A correction, determined by a blank experiment under the same conditions, is then applied.) The filtrate was found to require 39.5 cc. $N/10$ thiosulphate for ''immediate'' iodine and 2.5 cc. for '' additional.'' The total active oxygen obtained from the products of hydrolysis amounted to 0.0028 gram-molecule of the original peroxide, while 0.00288 gram-molecule had been taken. The loss is due to the instability of the solution of peracid. The per cent of active oxygen which separated as benzoic peroxide was 24.7.

2. 0.5100 gram was added to 100 cc. water and the previous experiment repeated. It was removed in thirty hours. 0.1416 gram benzoic peroxide was formed. The solution required 43.8 cc. $N/10$ thiosulphate. The total active oxygen recovered amounted to 0.00277 gram-molecule, while 0.00283 gram-molecule had been used. The per cent represented by benzoic peroxide was 20.6.

3. 0.6211 gram was shaken with 250 cc. water, twenty-four hours being necessary to complete the change. 0.1510 gram benzoic peroxide was formed. The solution required 54.8 cc. $N/10$ thiosulphate. A total of 0.00336 gram-molecule was recovered while 0.00345 had been used. 18.1 per cent of the active oxygen separated as benzoic peroxide.

It will be noted that the amount of benzoic peroxide formed

is decreased by using more water. From this it may be inferred that the rate of formation of this substance increases as the process progresses.

Further Examination of the Solution.—From previous work we might expect the solution to contain either benzoperacid or acetperacid, or both, together with hydroperoxide.

0.6035 gram of pure peroxide was shaken with 50 cc. water at 25° for two and one-half days, the change being complete in this time. The solution was then filtered from the benzoic peroxide, cooled to 15°, and 2 grams acetic anhydride added and dissolved by shaking. The solution was kept cooled to 15° and soon became turbid, owing to the separation of an oil. On scratching the side of the vessel with a glass rod, the oil solidified and separated at the bottom as crystals. After standing for one-half hour the supernatant liquid became perfectly clear, and the addition of more acetic anhydride produced no further separation. The crystalline product was separated from the solution and was found to consist of pure benzoic acetic peroxide. The crude substance melted at 37° to 38°; recrystallized at 38° to 39°. 0.1496 gram required 16.6 cc. N/10 thiosulphate; calculated 16.6 cc. A solution of benzoperacid, treated with acetic anhydride under the same conditions, showed the same formation of benzoic acetic peroxide. The formation of the latter in the hydrolyzed solution is, therefore, accounted for by the presence of benzoperacid.

$$C_6H_5CO.OO.H + (CH_3CO)_2O =$$
$$C_6H_5CO.OO.COCH_3 + CH_3COOH.$$
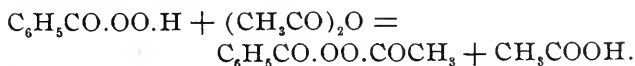
The filtrate from the crystalline peroxide was allowed to stand an hour for the hydrolysis of unchanged acetic anhydride, and was then extracted three times with one-third volume of pure ether in order to remove all benzoic acetic peroxide or benzoic acid, and any unchanged benzoic peracid. The ethereal solution was then treated with sodium carbonate solution which was added until, after shaking thoroughly, it remained permanently alkaline.

The ethereal solution, on evaporation, left a small amount

of residue having the very penetrating odor of acetic peroxide. This would indicate the presence of acetperacid in the original solution, were it not true that this solution contained a small amount of hydroperoxide. The alkaline extract was acidified and extracted thoroughly with ether. On evaporation there remained a residue of less than 0.02 gram of benzoic acid. A blank experiment, in which 0.1 gram of benzoic acid was subjected to exactly the same treatment, resulted in its complete recovery. A solution of benzoperacid, on standing, slowly changes to benzoic acid. As the above solution had stood two and one-half days and contained considerable benzoperacid, the presence of the small amount of benzoic acid obtained is easily accounted for, and it may be concluded that the primary hydrolysis of the peroxide results in the formation of no benzoic acid. This experiment also illustrates the ease with which a peracid in aqueous solution may be acetylated, and so completely removed from the acid accompanying it.

Benzoic acetic peroxide, therefore, hydrolyzes according to the following equation :

$$C_6H_5CO.OO.COCH_3 + H_2O = C_6H_5CO.OO.H + CH_3COOH.$$
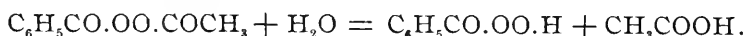
The possible hydrolysis into acetperacid and benzoic acid is excluded, or extremely minimized by the absence of benzoic acid.

From the three quantitative experiments previously detailed, it can be seen, however, that the total amount of peracid in solution is much in excess of the possible amount of benzoperacid, taking into consideration the amount of benzoic peroxide which has been formed. From this it might be concluded that the solution contains acetperacid. The presence of the latter may be explained by the following reaction :

$$C_6H_5CO.OO.COCH_3 + C_6H_5CO.OO.H =$$
$$C_6H_5CO.OOCO.C_6H_5 + CH_3CO.OO.H.$$
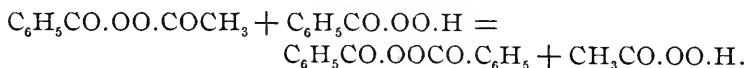
This would also explain the formation of benzoic peroxide. The formation of the latter might also be explained by the action of benzoperacid on benzoic acid, and this explanation is suggested by the absence of benzoic acid. We have found,

however, that benzoperacid and benzoic acid remain together in solution indefinitely without the formation of a trace of peroxide, which would be recognized by its precipitation.

The following facts leave no doubt as to the accuracy of the explanation given. As already noted, a solution of benzoic acetic peroxide becomes turbid on standing. If a few drops of dilute sulphuric acid be added to the solution this turbidity is prevented. If, besides the acid, a solution of benzoperacid be added, the turbidity appears under exactly the same conditions where, without the peracid, it is prevented. This fact shows that the latter is a factor in the formation of the benzoic peroxide. Furthermore, from the analogy between peroxides and anhydrides which this work has brought out, and from the reactivity of peracids and anhydrides, it might be expected that the former would also react with peroxides. The fact, already noted, that the amount of benzoic peroxide formed increases with the use of less water, is to be attributed to the increased concentration of the benzoperacid.

If a freshly prepared solution of acetic peroxide be treated with a solution of benzoperacid, the solution quickly becomes turbid, owing to the separation of benzoic acetic peroxide. The hydrolyzed solution of acetic peroxide, of course, does not show this behavior.

A drop or so of acetic acid has the same effect in preventing, or at least retarding, the formation of benzoic peroxide. If benzoic acetic peroxide be hydrolyzed in 5 per cent acetic acid, the formation of benzoic peroxide is altogether prevented. Such a solution, after standing three weeks, was evaporated in vacuum. The residue had a penetrating peracid odor and dissolved completely in sodium carbonate. There was, therefore, no benzoic peroxide formed, and none of the original peroxide remained unchanged. From these facts it further appears that the peracid owes its reactivity to its ion rather than to the undissociated molecule.

Hydrolysis of Other Peracids.

The behavior of aqueous solutions of benzoic peracid and phthalic monoperacid was also investigated.

Benzoperacid was prepared by Baeyer by the action of sodium ethylate on benzoic peroxide. As the substance can be preserved only a short time, it is best prepared in small quantities for experimental purposes in the following way : 24 grams of benzoic anhydride were pulverized and added to a solution of 11 grams potassium hydroxide in 250 cc. of 2.6 per cent hydroperoxide, cooled to 0°. After shaking for five minutes, the anhydride had gone into solution and a considerable amount of flocculent benzoic peroxide had been formed. This was removed by filtering through glass wool. The filtrate was then acidified with cold, dilute sulphuric acid and extracted twice with a small quantity of chloroform. On evaporating the solvent a residue of 11 grams remained, of which 2.8 grams were benzoperacid.

The solution, in accord with previous experience, was found to change slowly to hydroperoxide and benzoic acid. The change was followed by comparing the immediate liberation of iodine in dilute acetic acid solution with the total liberation. The change was found to take place much more rapidly in a dilute sulphuric acid solution (1 per cent), which indicates the hydrolytic nature of the process. The solutions were allowed to stand at room temperature. The numbers given in the tables represent cc. of N/10 thiosulphate required by 10 cc. of the solution.

The solution in sulphuric acid was treated with sufficient sodium acetate to neutralize it before estimating the "immediate" iodine.

Time in days.	Immediate.	Total.
0	9.6	9.6
10	8.2	8.7
20	7.2	8.0
30	5.9	6.9

Acidulated Solution.

0	9.6	9.6
10	4.9	8.7
20	3.1	8.4
30	1.6	8.1

Both solutions are ultimately changed completely into hy-

droperoxide, as indicated by the action on potassium iodide and the complete loss of odor. Furthermore, on saturating a 10 per cent solution of hydroperoxide with benzoic acid it is impossible to detect the formation of any peracid.

The phthalic monoperacid of Baeyer was found to undergo the same change with much greater rapidity. When in solution one-half of this substance ($N/2$ in active oxygen) was found to be changed in twenty-four hours. At the end of four days the change was complete.

This investigation was undertaken at the request of Professors Freer and Novy of the University of Michigan, whose article, "The Foundation, Decomposition, and Germicidal Action of Benzoyl Acetyl and Diacetyl Peroxides," has already been referred to. In the article of Freer and Novy are contained certain views concerning the hydrolysis of benzoic acetic peroxide which were held at that time, but which it has been found necessary to modify somewhat.

Univ. of Michigan, Laboratory
of General Chemistry.

XCIX.—ON THE IODIDES OF CAESIUM.

By H. W. Foote.

The periodides of caesium have been described by Wells[1] and by Wells and Wheeler,[2] who prepared the compounds CsI_3 and CsI_5. The object of the present investigation has been to show, primarily by means of solubility determinations, that these polyiodides and no others exist, at least within the range of temperatures investigated.

If water be brought in contact with an excess of any two caesium iodides, which can exist together, or with one iodide and iodine, the solubility of the mixture will have a certain definite value for any one temperature. This becomes evident by applying the phase rule,

$$v = C + 2 - P,$$

where v represents the number of physical conditions which

[1] Am. J. Sci., **43**, 17 (1892).
[2] *Ibid.*, **44**, 42 (1892).

may be varied, as concentration, pressure, and temperature, C the number of components making up the system, and P the number of phases. There are three components in the system, caesium iodide, iodine, and water, and four phases, consisting of the two iodides, or an iodide and iodine, solution and vapor. Hence,

$$v = 3 + 2 - 4 = 1,$$

or the system is monovariant. If the temperature be fixed, the solubility will adjust itself accordingly. Under working conditions the case is somewhat different theoretically. Here the vapor phase may be disregarded, leaving three phases, and we have

$$v = 3 + 2 - 3 = 2.$$

The system is under constant atmospheric pressure, however, fixing one of the variable conditions, and if the temperature be chosen as the other, the solubility will adjust itself as before. As solubility varies but slightly with great variations in pressure, the solubilities of the iodides under the vapor pressure of the solution or under atmospheric pressure are practically identical. In applying the phase rule below, it will be assumed that the system exists under its own vapor pressure with the vapor phase present.

While the solubility for any temperature is fixed, provided there is an excess of the solid phases, it will change as soon as the solid phases change their composition. Starting, then, at a given temperature from a solution of caesium iodide in water with excess of solid caesium iodide, if enough iodine be added to combine with a part of the caesium iodide to form the first periodide, the solubility will remain constant as long as these two iodides are present in the solid form. By adding enough iodine to combine with all the caesium iodide to form the first periodide and the next higher one, the solubility will be different from the first, but it will remain constant as long as these two iodides are present, without regard to the relative amounts. It will change only when the periodides change in composition. It may be taken as proof that the iodides have not changed in composition if the saturated

solutions remain constant throughout. When the composition of the saturated solution changes, it is proof that at least one solid phase has changed. By properly varying the quantities of iodine and caesium iodide and determining the solubility of each mixture, we can determine the number of different iodides which are capable of existing at any one temperature.

If the solution saturated with two iodides be cooled to the freezing-point, ice will separate. Five phases are then present, ice, the two iodides, solution and vapor, and the system becomes non-variant. Such a system can exist only at its cryohydric temperature, and the composition of the solution is fixed. When the composition of the iodides changes, the cryohydric temperature may change and the composition of the solutions will change. Here, again, we have a means of determining the number of iodides existing.

Caesium triiodide was prepared by treating a hot solution of caesium iodide with about half the calculated quantity of iodine, filtering, and allowing the solution to crystallize. A very beautiful product of the triiodide was obtained in this manner. In carrying out the experiments which have been outlined above, mixtures of caesium iodide and finely powdered iodine, or of caesium triiodide and iodine, were used. The mixture was usually heated for some time with water at as high a temperature as was practicable, and then allowed to cool and crystallize, so that no free iodine should remain in case combination was possible. The mixtures in definite amounts were treated with known quantities of water, so that the composition of the undissolved iodides could be calculated approximately, when the solubility of the mixture in water was found. The proportions of iodine were varied as much as possible. If, for instance, the solubility of a mixture of caesium triiodide and caesium pentaiodide was desired, two or more mixtures were made up in such proportions that the composition of the undissolved residue varied as much as possible between the composition of caesium triiodide and that of caesium pentaiodide. If no intermediate iodide exists, the solubility should be the same no matter what the proportion

of CsI_3 and CsI_5 may be. In case an intermediate iodide is present, as CsI_4, we should expect one value for the solubility when the composition of the residue falls between CsI_3 and CsI_4, and a different value when the composition is between CsI_4 and CsI_5.

Solubility determinations on the mixtures described were carried out usually in test-tubes which were placed in a thermostat. The mixtures were stirred continually for some hours by means of a flattened glass rod, which dipped to the bottom and was kept revolving by means of a turbine attachment. Sometimes the solutions were first prepared at a higher temperature and then placed in the thermostat and stirred. The results were practically the same whichever method was used. When the solutions were saturated, a quantity of the liquid was drawn off directly into a weighed specimen-tube, through a tube provided with a plug of glass wool to act as a filter. At the higher temperatures the tube was first warmed before being dipped in the liquid. The solution was weighed and transferred to a measuring-flask, and aliquot portions used to determine caesium iodide and iodine. The former was determined by evaporating the solution to dryness in a small porcelain dish and heating very slightly over a flame, the latter by titration with sodium thiosulphate.

The solubility determinations at the cryohydric temperatures, and for $35°.6$ and $52°.2$, are given in Table I. The solubilities are expressed in parts by weight of caesium iodide and iodine in 100 parts by weight of solution. Column (1) represents the solubility of pure caesium iodide; column (2), the solubility of a mixture of caesium iodide and caesium tri-iodide, *i. e.*, the solubility of a mixture of iodides containing more than 50.58 per cent of caesium iodide in the undissolved residue, this value being the percentage of caesium iodide in CsI_3. Should the solubility change as the percentage of caesium iodide in the undissolved residue changes, it would indicate that one or more intermediate iodides, as CsI_2 exist. The fact that the values obtained are practically constant, although the percentage of caesium iodide was varied largely, shows that no intermediate iodide forms. In the same way,

column (3) represents the solubility of mixtures of CsI_3 and CsI_5, *i. e.*, the solubility of mixtures containing between 50.58 and 33.85 per cent of caesium iodide in the undissolved residue, the latter value being the percentage of caesium iodide in CsI_5. Here, again, although the mixtures varied largely in composition, practically constant results show that intermediate iodides do not exist. Finally, column (4) gives the solubility of mixtures of CsI_5 and I, *i. e.*, of mixtures containing less than 33.85 per cent of CsI in the undissolved residues.

Table I.—Solubility of Caesium Iodides.

Temperature.	(1) Pure CsI. CsI. Per cent.	(2) CsI and CsI_3. CsI. Per c't.	I. Per c't.	(3) CsI_3 and CsI_5. CsI. Per c't.	I. Per c't.	(4) CsI_5 and I. CsI. Per c't.	I. Per c't.
Cryohydric	27.73	27.53	0.09	3.14	0.25	0.88	0.35
	27.64	27.51	0.09	3.59	0.35	0.84	0.34
$T = -4°.0$		$T = -4.°0$		2.82	0.35	0.83	0.34
				$T = -0°.4$		$T = -0°.2$	
$35°.6$	51.35	51.49	0.71	10.67	1.75	3.66	1.47
	51.61	51.84	0.71	10.78	1.86	3.82	1.73
$52°.2$	....	....	...	16.51	4.34	6.45	3.52
				17.06	4.70	6.99	3.13
						6.87	3.29
						6.44	3.61

The fact that the values in the above table are practically constant within the limits mentioned shows that other iodides do not form.

A dilatometer was filled with a mixture of caesium penta-iodide and iodine with a small quantity of water. The increase in volume was noted as the bulb was heated in a large water-bath. A sudden increase in volume was noted at $51°.5$, and it was found that the mixture melted, forming a heavy liquid at the bottom of the dilatometer, over which was the aqueous solution. The following two sets of readings were taken to establish this temperature. The first (Table II.) in order to obtain the approximate melting-point, and the second set (Table III.) to fix it accurately:

Table II.

Dilatometer scale.	Temperature.
1.40	$25°.1$
2.13	$29°.9$
2.99	$34°.85$
4.09	$40°.4$
5.09	$45°.1$
6.20	$49°.9$
23.90	$52°.7$

Table III.

Dilatometer scale.	Temperature.
3.30	$50°.9$
11.5	$51°.6$
2.2	$51°.4$
11.7	$51°.6$

The true melting-point was therefore taken to be $51°.5$.   At this temperature there are five phases, iodine, caesium penta-iodide, heavy liquid, aqueous solution and vapor, and three components.   The system is thus non-variant and it can exist only at this temperature.   Each liquid phase will have a definite composition, whatever the proportions of caesium penta-iodide and iodine.   On raising the temperature, one phase will disappear and the system will become monovariant again. Under ordinary conditions, either the caesium pentaiodide or iodine will melt completely when the temperature is raised, depending on which is in excess, and there will be either the monovariant system caesium pentaiodide, heavy liquid, aqueous solution, and vapor, or iodine, heavy liquid, solution and vapor.   The composition of the solutions in either system for any one temperature will be fixed irrespective of the relative quantities of each phase, but the solutions in the two systems will not have the same composition.

The composition of the heavy liquid from the mixture of caesium pentaiodide and iodine was determined by means of the apparatus shown in Fig. I.   AB is a glass rod ground at B to fit tightly into the large outer tube.   The latter is drawn out below and passes through a stopper into a weighed speci-men-tube.   Through the other hole in the stopper a tube passes as indicated.   The mixture of iodine and pentaiodide

with water is placed in the outer tube and
the apparatus placed in a thermostat, so that
the water comes nearly to the top of the outer
tube. The mixture is stirred thoroughly,
and when the solution is saturated the rod
AB is loosened, and by sucking at C the heavy
liquid is drawn through into the specimen-
tube and can then be analyzed. A plug of
glass wool is placed in the narrow tube open-
ing into the specimen-tube to serve as a filter
for the heavy liquid.

In Table IV., the solubilities of mixtures
of caesium triiodide and pentaiodide, and of
the pentaiodide and iodine are given for 52°.2
and 72°.6. The solubilities at 52°.2 are partly
taken from Table I. The lower temperature
is practically the same as the melting-point of
caesium pentaiodide and iodine under water,
and it will be noticed that the solubility of the
pentaiodide and iodine is the same whether

Fig. I.

caesium pentaiodide or iodine is present in excess. At 72°.6
the solubility of this mixture depends on which solid phase is
present. The same is also true in regard to the composition of
the heavy liquid which forms. At the melting-point the com-
position is fixed. At higher temperatures it depends on which
phase is present. The actual percentages of caesium iodide and
iodine are given as before. Column (1) shows the composi-
tion of solutions saturated with CsI_3 and CsI_5 ; column (2),
the composition of solutions in which CsI_5 is the solid phase ;
and column (3), the composition of solutions with iodine as
the solid phase.

A dilatometer filled with excess of caesium triiodide and
pentaiodide, moistened with water, showed no melting-point
when heated above 90°.

It was noticed by Wells and Wheeler[1] that various mix-
tures of caesium pentaiodide and iodine all melted at the same
temperature, about 73°. At this temperature there would be

[1] *Loc. cit.*

Table IV.—Solubility of Caesium Iodides.

Temp.	(1) Solid phases = CsI_3 and CsI_5		(2) Solid phase = CsI_5				(3) Solid phase = I			
			Solution.		Heavy liquid.		Solution.		Heavy liquid.	
	CsI.	I.	CsI.	I.	CsI.	I.	CsI.	I.	CsI.	I.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
52°.2	16.51	4.34	6.45	3.52	22.94	73.72	6.87	3.29	22.80	74.63
	17.06	4.70	6.99	3.13	....	....	6.44	3.61	....	....
72°.6	27.03	14.72	16.51	10.86	27.12	68.48	6.40	4.18	17.68	80.02
	26.94	15.43	16.82	10.15	28.01	68.34	6.14	3.98	....	....

four phases present, caesium pentaiodide, iodine, liquid and vapor, and two components, caesium iodide and iodine. The system would, therefore, be non-variant and the composition of the liquid formed at this temperature should be constant, regardless of the proportions of caesium pentaiodide and iodine, provided both be present.

To test this point, mixtures of cae-sium pentaiodide and iodine were made in various proportions by melt-ing together caesium triiodide and iodine. The mixtures were placed in the bulb A of the tube (Fig. II.), the lower opening being closed with a platinum cone and glass wool to act as a filter. The tube was placed in a bath and heated till the mixture be-gan to melt. By slight suction at B the melted liquid was drawn into the bulb C. The tube was then removed from the bath and the material in C broken out carefully and analyzed. Three determinations were made in this manner. The mixtures were always heated somewhat above the temperature where melting began in order to get liquid enough to analyze. The following results were obtained:
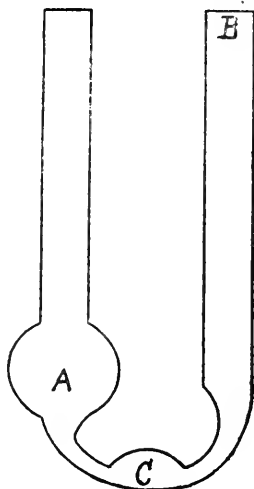
Fig. II.

Table V.

(Caesium pentaiodide contains 33.85 per cent CsI.)

	Percentage CsI in mix-ture.	Percentage CsI found in liquid.	Temperature at which melt-ing began.	Temperature at which liquid was drawn over.
1	29.96	20.20	73°	77°–78°
2	19.96	18.87	73°	"
3	10.29	18.03	73°.5	79°

The results in the second column agree as well as could be expected and show that the composition of the melted liquid is practically constant. This serves as further proof that iodides higher than CsI_5 do not exist at this temperature, for if a higher iodide did exist it should form a liquid with iodine

having a composition different from that above and with a different freezing-point.

In the preceding article it has been shown, chiefly by means of solubility determinations, that caesium triiodide and caesium pentaiodide are the only periodides of caesium existing between —4° and 73°. The phase rule has served as a guide throughout and the results obtained agree in all cases with the theoretical conclusions.

NEW HAVEN, CONN., Oct., 1902.

ON CERTAIN DERIVATIVES OF PICRIC ACID.[1]

BY C. LORING JACKSON AND R. B. EARLE.

The following paper contains a description of some new compounds, not of much importance, which were prepared in our work upon the colored addition-compounds formed from sodic alcoholates and nitro derivatives of benzol.

Picryl Bromide (*1-Brom-2,4,6-trinitrobenzol*), $C_6H_2Br(NO_2)_3$. —This substance was prepared in the hope that it would lead to trinitroanisol with less trouble than the common way of making it from picryl chloride. The yield, however, was so small that the method did not prove of value. The process for making trinitroanisol from anisic acid, on the other hand, gave excellent results, and is described in our paper on the colored addition-compounds.

Twenty-five grams of 1-brom-2,4-dinitrobenzol were added to a mixture of 500 cc. of fuming nitric acid, of sp. gr. 1.51, and 200 cc. of fuming sulphuric acid, of sp. gr. 1.86, and the whole boiled vigorously for about three hours in a flask closed with a glass bulb. At the end of this time most of the nitric acid had been driven off, and the liquid ceased to boil quietly, but began to effervesce slightly and to give off very dark red fumes. It was then allowed to cool, poured into a large volume of ice-water, and the precipitate formed dried on a porous plate to get rid of adhering oily impurities. The solid

was recrystallized from a mixture of alcohol and benzol until it showed the constant melting-point 122° to 123°, when it was dried at 100° and analyzed with the following result :

0.2820 gram substance gave, by the method of Carius, 0.1824 gram argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_3$.	Found.
Br	27.37	27.52

The yield was small, not more than 25 per cent of the theoretical, which we ascribe to oxidation during the long boiling, but, if an attempt was made to check this by diminishing the length of the boiling, little or none of the substance was formed. That it is really the picryl bromide was proved by its conversion into trinitroanisol, melting-point 64°, by treatment with sodic methylate.

Properties of Picryl Bromide.—It crystallizes from alcohol in large, yellowish-white crystals, consisting of long plates terminated at each end by two planes at an acute angle, which is often truncated. Rhombic plates were also observed. Frequently arborescent, frost-like groups occur, with many branches set obliquely to the trunk and each branch bordered with rhombic plates, giving it a jagged outline. It melts at 122° to 123°, and is freely soluble in benzol or acetone ; soluble in alcohol, cold or hot, chloroform, ether, methyl alcohol, glacial acetic acid, or carbonic disulphide ; slightly soluble in cold, soluble in hot ligroin ; insoluble in water. The strong acids do not act upon it even when hot, nor do cold alkalies affect it, but it is easily attacked by hot solutions of an alkali. Sodic methylate converts it into trinitroanisol, as has been already stated. The best solvent for it is a mixture of alcohol and benzol.

Phenyl Picrate, $C_6H_2(NO_2)_3OC_6H_5$.—A solution of sodic phenylate was prepared by dissolving 0.4 gram of sodic hydrate in 1.2 grams of phenol mixed with a little water ; 2.6 grams of picryl chloride were then added to this solution in small quantities at a time, stirring the liquid constantly during the addition. The mass soon took on a dark color, and much heat was developed. On washing the product with

water, a dirty, insoluble mass was obtained, which was crystallized from a mixture of alcohol and benzol until it showed the constant melting-point, 153°, when it was dried at 100° and analyzed with the following result :

0.1676 gram substance gave 20.2 cc. N at 20° and 769.3 mm.

	Calculated for $C_6H_2(NO_2)_3OC_6H_5$.	Found.
N	13.77	13.96

Properties of Phenyl Picrate.—It crystallizes from a mixture of alcohol and benzol in yellowish, short, thick prisms, probably of the monoclinic system, which are terminated by two planes at an obtuse angle. It melts at 153° and is freely soluble in benzol or acetone ; soluble in methyl or ethyl alcohol, chloroform, or cold glacial acetic acid, freely soluble in the last when hot ; slightly soluble in ether ; insoluble in water or ligroin. The best solvent for it is a mixture of alcohol and benzol. Willgerodt[1] prepared this substance but gives no description of it.

Action of Acetoacetic Ester on Phenyl Picrate.—In an earlier paper[2] from this laboratory it was shown that the phenoxy groups in dichlordiphenoxyquinone were easily replaced by malonic ester residues, in fact this gave the best method of preparing the dichlorquinonedimalonic ester. The following experiment was tried to see whether the phenoxy group in the phenyl picrate would also be susceptible of replacement : A solution of sodic acetoacetic ester was prepared by adding 0.22 gram of acetoacetic ester to the solution of sodic ethylate from 0.04 gram of sodium and absolute alcohol, and to this was added a benzol solution of 0.5 gram of phenyl picrate. The mixture took on a deep-red color almost immediately, but we do not feel certain whether this was due to the salt of the picrylacetoacetic ester or to the formation of an addition-product (salt of a quinolnitro acid). The mixture was allowed to stand twenty-four hours at ordinary temperature, after which it was washed with water in a separating-funnel and the aqueous washings acidified with dilute hydrochloric

---

[1] Ber. d. chem. Ges., **12**, 1278 (1879).
[2] This JOURNAL, **17**, 597.

acid. The oily precipitate thus obtained was redissolved in sodic hydrate, filtered and acidified once more. As the precipitate was still gummy, it was extracted with carbonic disulphide, the extract evaporated to dryness, washed with a little cold alcohol, and recrystallized from alcohol until it showed a constant melting-point. As this lay at 97° to 98° there can be no doubt that the substance is the trinitrophenylacetoacetic ester discovered by Dittrich,[1] and that the phenoxy group is easily replaced by the acetoacetic ester residue.

4-Brom-2-nitrophenyl Picrate, $C_6H_2(NO_2)_3OC_6H_3BrNO_2$.— Two grams of the sodium salt of 4-brom-2-nitrophenol were dissolved in 50 cc. of hot alcohol and 2 grams of picryl chloride were added to the solution in small portions at a time, with constant stirring. The heavy, yellow, crystalline precipitate formed was filtered out, washed with water, and recrystallized from acetone, until it showed the constant melting-point, 232°, when it was dried at 100° and analyzed with the following result :

0.2009 gram substance gave, by the method of Carius, 0.0885 gram argentic bromide.

	Calculated for $C_6H_2(NO_2)_3OC_6H_3NO_2Br$.	Found.
Br	18.63	18.75

Properties of 4-Brom-2-nitrophenyl Picrate.—It crystallizes from acetone in short, thick prisms, probably belonging to the monoclinic system, terminated at each end by two planes at an obtuse angle to each other. Its color is yellowish-white, and it melts at 232°. It turns brown on exposure to the air. It is freely soluble in hot acetone, soluble in it when cold ; soluble in hot benzol, slightly soluble in cold ; slightly soluble in ethyl or methyl alcohol, chloroform, ether, or glacial acetic acid ; insoluble in water or ligroin. The best solvent for it is acetone. It seems to form a colored addition-compound with sodic acetoacetic ester, but this may be instead the red salt of picrylacetoacetic ester, as pointed out in the last section.

[1] Ber. d. chem. Ges., **23**, 2720 (1890).

ON SYMMETRICAL DINITROBENZOLSULPHONIC ACID.[1]

By C. Loring Jackson and R. B. Earle.

In the course of our work on the colored addition-compounds derived from nitrobenzols and sodic alcoholátes (quinolnitro acids) it became desirable to study the behavior of the symmetrical dinitrobenzolsulphonic acid, but on looking up the literature we could find no description of this substance. Limpricht[2] had prepared an acid by the action of nitric and sulphuric acids on metanitrobenzolsulphonic acid, to which this constitution would naturally be assigned, but Sachse,[3] who studied it more fully, determined its structure as $(NO_2)_2 1, 2, SO_3 H 3$.

We therefore prepared the symmetrical dinitrobenzolsulphonic acid from the dinitroaniline obtained from symmetrical trinitrobenzol by decomposing the diazoethylxanthogenate and oxidizing the product. As none of these processes could have produced a molecular transformation, there is no doubt that our acid is the symmetrical dinitrobenzolsulphonic acid. This acid proved itself identical with the acid of Limpricht and Sachse, just mentioned, as appears from the following comparison :

	Our acid.	Limpricht.
Melting-point of chloride	$98°–99°$	$97°$
" " amide	$234°–235°$	$235°$

Sachse found $89°$ for the chloride and $238°$ for the amide. The barium salt from each acid crystallizes with 3 molecules of water, and for greater certainty its solubility was determined with a salt made from our acid and with one from an acid made by the method of Limpricht and Sachse.

One hundred parts of water at $20°$ contain the following number of parts of the salt free from water of crystallization :

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Science, by R. B. Earle.

[2] Ber. d. chem. Ges., 9, 554.

[3] Ann. Chem. (Liebig), 188, 143 (1877).

Our salt.		Sachse's salt.	
4.41	4.39	4.45	4.37

There can be no doubt, therefore, that Sachse made some mistake in his work on the constitution of his acid, since it is evidently the symmetrical and not the vicinal isomer. Sachse's work consisted in reducing the dinitro acid to a diamidobenzolsulphonic acid, replacing each amido group by an atom of bromine by the diazo reaction, and comparing the melting-points of the chloride and amide of this dibrombenzolsulphonic acid with those of the three isomers already known. As they coincided with none of these, it followed that the substance was the only remaining isomer, the as yet undiscovered 1,2-dibrom-3-sulphobenzol. We have followed Sachse's constitutional work as closely as possible, but, unfortunately, the amount of substance at our disposal was too small to give perfectly definite results, and it was too late to prepare more of this acid, which requires heating with nitric acid for fourteen days. The diamidobenzolsulphonic acid obtained by us showed the characteristic crystalline form described by Sachse. The dibrombenzolsulphonic acid was converted into the chloride, but showed no signs of solidifying after standing for a week. It was accordingly converted into the amide, which melted at 203° three times in succession during its recrystallization from alcohol, the residue from the mother-liquors of the last crystallization melted at 202° to 203°, and there was not enough substance left for another crystallization. We compare below the melting-points given by Sachse, those of the chloride and amide of the 1,3-dibrom-5-sulphobenzol determined by Lenz,[1] and our result :

	Sachse.	Lenz.	Our result.
Chloride	127°	57°.5	. . . .
Amide	215°	203°	203°

While it is improbable that a chloride melting at 127° would remain obstinately liquid, as ours did, this behavior would be expected in summer from a chloride melting at 57°. On the other hand, a determination of the solubility of our amide did not agree with that given by Lenz, as he found

[1] Ann. Chem. (Liebig), **120**, 158.

0.0958 gram of the substance in 100 grams of solution at 18°, while we found 0.0061 and 0.0060. The probable reason for this discrepancy is that he allowed his amide to stand with the water eleven days, when partial decomposition might have taken place, while our determination was carried through in two hours. Our experimental results then do not settle finally the dibrombenzolsulphonic acid made from Sachse's dinitrobenzolsulphonic acid, but they make it highly probable that it is identical with Lenz's 1,3-dibrom-5-sulphobenzol. Fortunately, however, this experimental proof is unnecessary, since our preparation of the dinitrobenzolsulphonic acid from symmetrical dinitroaniline has proved that its structure is $(NO_2)_2 1,3,SO_3H5$, and, therefore, that Sachse's dibrom acid is identical with that of Lenz in spite of Sachse's different melting-points. How Sachse made this mistake in the melting-points of his chloride and amide we are unable to explain, especially as his paper gives evidence of very careful work. They fall near those of the 1,2,3-tribrom-5-sulphobenzol derivatives[1] (Sachse: 127° tribrom, 127° for the chloride, 215° and 210° for the amide), but that Sachse had these tribrom compounds in hand is disproved by his numerous analyses of the salts of the acid.

The result of our work is that the dinitrobenzolsulphonic acid of Limpricht and Sachse is the symmetrical isomer, $(NO_2)_2 1,3,SO_3H5$, and therefore the vicinal acid $(NO_2)_2 1,2, SO_3H3$ still remains to be discovered.

<div align="center">EXPERIMENTAL PART.</div>

Preparation of 1,3-Dinitro-5-sulphobenzol, $C_6H_3(NO_2)_2SO_3H$, from Symmetrical Dinitroaniline.

Ten grams of 1,3,5-dinitroaniline (made from trinitrobenzol[2]) were dissolved in hot hydrochloric acid (one part of strong acid to one of water). The solution was filtered hot, allowed to cool, and treated with 14 grams of sodic nitrite (a large excess over the amount needed by the theory), which was added in small portions at a time, the flask being cooled by running water after each addition. The solution soon became

[1] Lenz: Ann. Chem. (Liebig), **181**, 29.

[2] Bader: Ber. d. chem. Ges., **24**, 1654 (1891).

filled with a dirty, brownish-red precipitate of the diazo chloride. As soon as all the nitrite had been put in, the liquid was diluted to 300 cc. with cold water, and a fresh solution of 15 grams of potassic ethylxanthogenate[1] in 100 cc. of cold water was added in small portions at a time, with constant shaking. During this addition the solution turned yellow, and a bright yellow precipitate of the diazoxanthogenic ester was formed, which floated on the surface. On warming the mixture to 80° the yellow solid was converted into a heavy brown oil, and nitrogen was given off. This oil was extracted with ether, and, after distilling off the ether on the water-bath, it was oxidized directly without any attempt at purification, or even saponification. For this oxidation nitric acid was used, beginning with a mixture of one part of strong acid with one of water to avoid too violent action. It was boiled with this diluted acid until it ceased to act with it, after which enough strong nitric acid was added to the boiling solution to start the oxidation once more, and this treatment was repeated until all the oil had dissolved and no more red fumes were evolved. The solution thus obtained was evaporated on the water-bath until the odor of nitric acid had gone, diluted with water, filtered, and the filtrate digested with baric carbonate until neutral. The tarry phenol, insoluble in water, was present in such small quantity that no attempt was made to identify it. The neutral barium salt was filtered off, and the washings of the insoluble barium salts having been added, the whole was evaporated to dryness on the steam-bath. For purification it was converted into the chloride, which will therefore be described next.

1,3-Dinitrobenzol-5-sulphochloride, $C_6H_3(NO_2)_2SO_2Cl$.—The crude barium salt prepared in the manner just described, after it had been dried on the steam-bath, was mixed in a test-tube with an equal weight of phosphoric pentachloride, and the mixture heated to 150°. At about 140° the reaction began. After it had ended, most of the phosphoric oxychloride was distilled off and the residue treated with cold water. The insoluble part was filtered out, dried *in vacuo*, and purified by dissolv-

[1] R. Leuckart: J. prakt. Chem., [2], **41**, 197 (1890).

ing it in chloroform, adding enough ligroin for precipitation, and allowing the mixture to stand, when the turbid solution gradually deposited large, yellowish crystals. These were freed from some tarry matter by washing with cold ether, after which the crystallization from chloroform and ligroin was continued until it showed the constant melting-point, 98° to 99°, when it was dried *in vacuo* and analyzed with the following result :

0.3245 gram substance gave, by the method of Carius, 0.1770 gram AgCl and 0.2788 gram $BaSO_4$.

	Calculated for $C_6H_3(NO_2)_2SO_2Cl$.	Found.
Cl	13.32	13.49
S	12.00	11.80

Properties of the 1,3-Dinitrobenzol-5-sulphochloride.—It crystallizes from chloroform and ligroin in good-sized, yellowish-white, flat prisms, apparently monoclinic or triclinic, the terminations being made up of two principal planes at an obtuse angle to each other, and forming oblique angles with the basal planes. They seem to be arranged in pairs diagonally across the prism. Usually the terminations are much modified, and occasionally develop lancet-shaped ends. As they grow larger they generally become much distorted. It melts at 98° to 99°, and is freely soluble in benzol, chloroform, or glacial acetic acid ; soluble in ether ; insoluble in water or ligroin. The best solvent for it is a mixture of chloroform and ligroin. It is comparatively stable in contact with hot water, but is decomposed by long boiling with it. Hot alcohol decomposes it rapidly, after it has dissolved it. Hot solutions of the alkalies decompose it very quickly.

1,3-Dinitrobenzol-5-sulphamide, $C_6H_3(NO_2)_2SO_2NH_2$.—This substance was prepared by treating the chloride with a small amount of strong ammonic hydrate and allowing the mixture to stand for a short time, after which it was diluted and the amide filtered off. It was purified by dissolving it in alcohol, adding an equal volume of hot water, and allowing it to crystallize out as the mixture cooled. The melting-point became constant at 234° to 235°. It forms short, slender prisms of a

yellowish color, and is soluble in hot alcohol ; soluble in hot water, practically insoluble in cold, yet it is more convenient to crystallize it from a mixture of hot alcohol and water than from water alone ; slightly soluble in ether, benzol, chloroform, glacial acetic acid, or ligroin.

Baric 1,3-Dinitrobenzol-5-sulphonate, $(C_6H_3(NO_2)_2SO_3)_2Ba.$ $3H_2O.$—The pure sulphochloride was boiled with water until the whole had dissolved, and the solution evaporated to dryness on the steam-bath, when the free acid separated in large, white crystals, contaminated with a dark-colored impurity. This acid was heated for two hours on the steam-bath to remove the last traces of hydrochloric acid, then dissolved in water, and treated with baric carbonate. The barium salt freed from the excess of carbonate by filtration, was evaporated until it began to crystallize, and purified by several recrystallizations from water. It was dried in the air and analyzed with the following result :

0.4392 gram air-dried salt lost, when heated to 120°, 0.0356 gram $H_2O.$

	Calculated for $(C_6H_3(NO_2)_2SO_3)_2Ba.3H_2O.$	Found.
H_2O	7.88	8.11

0.2496 gram salt, dried at 120°, gave 0.0912 gram $BaSO_4.$

	Calculated for $(C_6H_3(NO_2)_2SO_3)_2Ba.$	Found.
Ba	21.71	21.48

Properties of the Barium Salt.—It crystallizes from water in masses of pale-yellow prisms, which lose part of their water of crystallization over sulphuric acid, and nearly all of it at 100°, but the last portions are given off very slowly at this temperature, so that it is wiser to heat to at least 120° in drying the salt. It is soluble in alcohol. Its solubility in water was determined as follows :

I. 8.9006 grams solution, at 20°, contained 0.3922 gram salt dried at 140°.

II. 11.0533 grams solution, at 20°, contained 0.4851 gram salt dried at 140°.

100 parts of the solution, at 20°, contained, therefore, the following numbers of parts of the anhydrous salt :

<div align="center">

I.   II.

4.41   4.39

</div>

The substance forms, with sodic methylate, a salmon-colored salt of a quinolnitro acid,

$$(C_6H_3(NO_2)_2SO_3NaOCH_3)_2Ba,$$

which has been described in another paper.   When moistened with benzol, chloroform, or ligroin, it takes on a deep-red color.   It is a decidedly stable substance for one of this class.

Preparation of Dinitrobenzolsulphonic Acid from Metanitrobenzolsulphonic Acid According to Sachse.[1]

This work was undertaken in order to make a more careful comparison of this acid with the one prepared by us, because the melting-points of the chlorides and amides pointed to the identity of the two.   The process was carried on as follows : Fifty grams of the metanitrobenzolsulphonic acid were boiled for fourteen days with a mixture of 300 cc. of fuming sulphuric acid, of 1.86 sp. gr., and 300 cc. of nitric acid, of 1.50 sp. gr., in a flask provided with a long air-condenser ground into its neck.   At the end of this time the mixture was allowed to cool, poured into a large volume of water, and heated in a dish over the water-bath for four days to get rid of the nitric acid, more water being added from time to time to replace that which evaporated.   The solution was then treated with an excess of baric carbonate (omitting the treatment with lime used by Sachse), and the barium salt evaporated to crystallization, the first crystals being rejected.   The red crystals, which separated from this crude solution, were recrystallized from hot water, when they lost this red color and became yellow, thus removing one of the differences between our acid and that described by Sachse.   The crystalline form of this barium salt was also similar to that of ours.   To be certain that it was Sachse's salt, it was analyzed with the following result :

0.2983 gram salt, dried at 120°, gave 0.1097 gram of $BaSO_4$.

	Calculated for $(C_6H_3(NO_2)_2SO_3)_2Ba$.	Found.
Ba	21.71	21.63

[1] Ann. Chem. (Liebig), 188, 143 (1877).

The determination of its solubility gave the following results :

I. 6.9690 grams solution, at 20°, contained 0.3098 gram salt dried at 140°.

II. 10.9542 grams solution, at 20°, contained 0.4790 gram salt dried at 140°.

100 parts of the solution, at 20°, contained, therefore, the following numbers of parts of the anhydrous salt :

I.	II.
4.45	4.37

These results prove that the two acids are identical.

Conversion of Sachse's Dinitrobenzolsulphonic Acid into Dibrombenzolsulphonic Acid.

In this part of the work, Sachse's method[1] for determining the constitution of his acid was followed. The reduction of the dinitro to the diamido acid was carried on with sulphuretted hydrogen. For this purpose the ammonium salt (prepared by the action of ammonic carbonate on the barium salt described in the preceding section) was dissolved in 200 cc. of water, mixed with 20 cc. of ammonic hydrate of the common laboratory strength, and treated with sulphuretted hydrogen for two hours. The liquid became hot, turned dark-brown, and deposited a large amount of sulphur. After boiling it to collect the sulphur in larger grains, it was filtered, concentrated, and while hot acidified with acetic acid. After standing for twenty-four hours, large, well-formed, yellowish-red crystals separated, which accord with Sachse's description of the diamidobenzolsulphonic acid, except that we should describe it as soluble rather than difficultly soluble in water. The amount of these crystals was small, and to obtain most of the diamidobenzolsulphonic acid we added an excess of strong hydrochloric acid to the mother-liquor, which threw down a heavy crystalline precipitate of the chloride, since this is but slightly soluble in strong hydrochloric acid. After one recrystallization from water the chloride was converted into the free acid by cautious addition of argentic carbonate, and this

[1] Ann. Chem. (Liebig), **188**, 148 (1877).

changed into the bromide with hydrobromic acid. The bromide, which is more soluble than the chloride, was recrystallized several times from water, but, as this failed to decolorize it completely, we proceeded to the conversion of it into the dibrombenzolsulphonic acid.

The acid, or its bromide, was suspended in freshly distilled hydrobromic acid, and treated for half an hour with a stream of nitrous anhydride (from arsenious anhydride and nitric acid). The liquid was then warmed until the evolution of nitrogen had begun, and after the reaction had spent its violence, heated to boiling. This treatment was repeated until no more nitrogen was given off. The hydrobromic acid was then driven off by warming on the steam-bath, water added, and the barium salt formed with baric carbonate, the solution being filtered hot. The highly colored product was decomposed with sulphuric acid and then again converted into the barium salt, which removed part of the colored impurity, leaving the salt of a light-brown color. The method is essentially the same as that of Sachse.

The baric dibrombenzolsulphonate was converted into the chloride by heating it in a test-tube with a large excess of phosphoric pentachloride (about equal weights of the two substances). The action began at about 100°, but the temperature was carried to 150° to finish the reaction. After most of the phosphoric oxychloride had been distilled off, the cool mass was treated with ice-water, which left the chloride as a brown oil, which did not solidify, even after long standing. Accordingly it was converted into the amide by ammonic hydrate in the cold, and this amide was recrystallized from alcohol. Unfortunately, the amount of material at our disposal was not sufficient to get an absolutely constant melting-point, but that we had nearly approached this point is shown by the following observations made after the last three crystallizations:

Melting-point of crystals.	Melting-point of evaporated mother-liquor.
203°	197°–201°
203°	200°–202°
203°	202°–203°

One more crystallization would undoubtedly have given a constant melting-point, but we did not have the material for it. Sachse[1] found the melting-point 215° for his amide made in precisely the same way. The melting-point of 1,3-dibrom-benzol-5-sulphamide is 203° according to Lenz.[2] In the hope of establishing the identity of Lenz's and our amides we determined the solubility of our amide as follows:

I. 87.5 grams solution, at 18°, contained 0.0053 gram substance.

II. 100 grams solution, at 18°, contained 0.0060 gram substance.

100 parts solution, at 18°, contain the following numbers of parts of the amide:

I.	II.
0.0061	0.0060

These results do not agree with the solubility determined by Lenz, which he puts at 0.0958. The difference is undoubtedly due to the fact that Lenz made his solution by soaking the amide for eleven days, during which time partial conversion into the ammonium salt is possible, whereas our solution was made in two hours. The subject is of too slight importance to make it worth while to undertake the work necessary to settle the point by more definite experimental results.

STUDIES IN NITRIFICATION.

By G. S. Fraps.

This article falls naturally into three parts, as follows:

Part I.—Variations in the nitrifying power of the same soil.

Part II.—The nature of the nitrifying organisms.

Part III.—Determination of the comparative nitrifying power of soils.

[1] Ann. Chem. (Liebig), **188**, 155 (1877).
[2] *Ibid.*, **120**, 158.

Variations in the Nitrifying Power of the Same Soil.

This portion of the study was undertaken primarily on account of serious irregularities observed in the nitrifying power of the same soil at different times during the course of work on other portions of this research. For example, a soil taken from a wheat field, May 28, nitrified 143 milligrams nitrogen per kilogram of soil in three weeks, while a second sample, taken three weeks later, nitrified only 20 milligrams under the same conditions.

The two ways in which the nitrifying power of a soil may be studied are as follows :

1. *The Rate of Nitrification in the Soil.*—The quantity of nitrates in the soil may be determined at the end of different periods of time, when the quantity formed per unit of time during each period is a measure of the rate of nitrification in the soil, or its energy of nitrification, as it will be called in this article. The initial energy of nitrification of a soil is measured by its rate of nitrification during the first period.

2. *The Inoculation Energy of the Soil.*—This is taken to mean the power of a soil to bring about nitrification in a sterilized soil which has been placed under proper conditions for nitrification. The measure of the nitrification energy of a given soil is the quantity of nitrates formed in a standard sterilized soil under standard conditions, and in a definite time.

As will be seen later, the nitrification energy of a soil and its inoculation energy are quite different.

The nitrifying power of a soil, meaning both its energy of nitrification and its inoculation energy, depends upon two factors, the number of nitrifying bacteria present and their activity.

The maximum number of nitrifying bacteria which may be contained in a soil, under field conditions, depends upon the nature of the soil itself, since some soils offer a much more favorable medium for the growth of the nitrifying organisms than others. This aspect of the question will be treated in

Part III. It also depends upon the nature and amount of crop residues, nitrogenous fertilizers, humus, and other nitrifiable matters which may be present. With decrease in the amount of food present, or its availability, it is obvious that the soil, aside from its nature, offers a much less favorable medium for the reproduction of the nitrifying bacteria.

The number of nitrifying bacteria in any given soil at any time will depend as much upon the conditions to which the soil is subjected as on its nature. According as favorable or unfavorable conditions prevail, the number of organisms in the soil will be greater or less. Cold, dryness of the soil, and excess of moisture will diminish their numbers, while warmth and a proper amount of moisture will be favorable to their increase. Evidently, the number of nitrifying organisms in any soil is subject to fluctuations, according to the season, and the weather to which it is exposed, and consequently we may expect to find that the nitrifying power of the soil is also subject to variations.

The activity of the nitrifying organisms also varies from time to time. If the rate of nitrification of ammonium sulphate or cottonseed meal is studied under uniform conditions of temperature and moisture, it is seen that the nitrification takes place in stages, a period of activity being preceded and followed by periods of inactivity. That is to say, the rate of nitrification is periodic. A study of the inoculation energy of soils also gives evidence of variations in the activity of the nitrifying organisms.

Variations in Energy of Nitrification.

The rate of nitrification of cottonseed meal and of ammonium sulphate was determined in a number of samples of soil, the measure being the quantity of nitrates formed per week during the first three weeks, and succeeding weeks. The method of work will be described later.

The curves in Fig. I. exhibit graphically the variations in the energy of nitrification with time. The curves were chosen to show how the period of greatest energy of nitrification may come during the first three weeks, the fourth week,
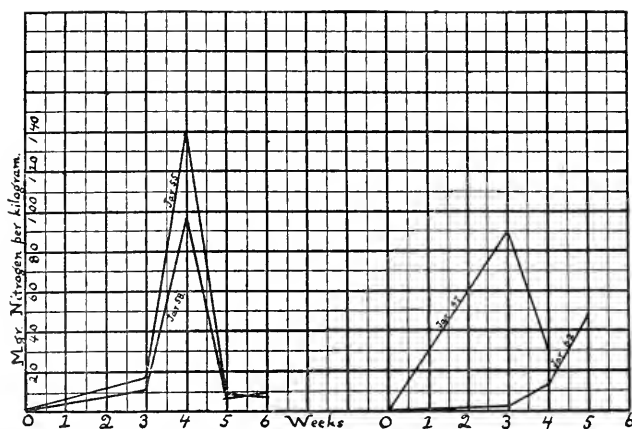
Fig. I.—Rate of nitrification of ammonium sulphate and cottonseed meal.

or the fifth week, according to the condition of the soil at the time of starting the experiment. The results of all the determinations are given in Table I.

Table I.—*Energy of Nitrification.*

		Milligrams nitrogen per kilogram soil oxidized per week.				
	Soil and nutrient.	Three weeks.	Fourth week.	Fifth week.	Sixth week.	Total.
Soil 1748	Inoculation tests					
Jar 55	Cottonseed meal	17	141	9	8	210
" 56	Ammonium sulphate	5	59	..	37[1]	138
" 57	Cottonseed meal	12	109	−57[2]	5	91
" 58	Ammonium sulphate	11	96	6	9	143
Soil 1764	Inoculation tests					
Jar 67	Cottonseed meal	2	94	34	..	133
" 68	Ammonium sulphate	2	53	18	..	69
Soil 1766	Inoculation tests					
Jar 72	Cottonseed meal	10	106	0	..	135
" 74	Ammonium sulphate	2	61	−9[2]	..	57
Soil 1772	Direct nitrification					
Jar 77	Cottonseed meal	2	63	..	..	70
" 79	Ammonium sulphate	1	1	0	..	4
Soil 1772	Inoculation tests					
Jar 81	Cottonseed meal	7	103	..	..	124
" 83	Ammonium sulphate	3	62	..	..	70

[1] Mean of fifth and sixth week.
[2] Dentrification took place.

| Soil and nutrient. | Milligrams nitrogen per kilogram soil oxidized per week. | | | | |
	Three weeks.	Fourth week.	Fifth week.	Sixth week.	Total.
Soil 1781 Inoculation tests					
Jar 91 Cottonseed meal	31	66	..	..	159
" 93 Ammonium sulphate	25	49	..	..	124
Soil 1781 Direct nitrification					
Jar 87 Cottonseed meal	90	30	..	..	300
" 90 Ammonium sulphate	93	39	3	..	319
Soil 1746 Direct nitrification					
Jar 47 Cottonseed meal	12	..	69[1]	42	218
" 49 Ammonium sulphate	7	..	28[1]	52	129
Soil 1768 Inoculation tests					
Jar 62 Cottonseed meal	1	13	67	..	83
" 65 Ammonium sulphate	2	9	64	..	79

The following statements appear justified by the figures given in the table :

1. The initial energy of nitrification is low in some cases (soils 1766, 1772) and high in others (soil 1781).

2. The rate of nitrification is periodic, reaching a maximum, and then decreasing. The decrease is not due to lack of nitrogen to nitrify, for the soil contains 0.532 gram of nitrifiable nitrogen per kilogram, and the total amount nitrified is less than half of this in most cases.

3. In a given soil, the period of greatest energy of nitrification comes at the same time, whether the nitrogen is supplied in the form of cottonseed meal or ammonium sulphate.

4. The period of greatest energy of nitrification has come, as a rule, in the fourth week. This is the case with six of the nine sets of soils in the table. In one set it came in the fifth week, in one set during the first three weeks, and one during either the fourth or fifth week.

Cause of the Variations.

The explanation of the variations in the rate of nitrification in soils is probably to be found in the life history of the organisms. There seems to be a period during which the germs multiply, and little nitrification takes place, then a short period of rapid nitrification, followed by a period of multiplication with little nitrification. How long a period of

[1] Mean of fourth and fifth week.

time it requires for the organisms to complete this cycle of changes cannot be stated. The maximum time required in any of the experiments here given for the maximum of activity of nitrification to occur was five weeks.

The life activity of the bacteria which assimilate nitrogen on the roots of legumes is also periodic. Cultivated outside of the plant, they assimilate nitrogen with difficulty, only 7 milligrams per gram of sugar consumed by them. When growing in nodules on legumes, according to Nobbe and Hiltner, they are purely parasites, until the bacteria are transformed into bacterioid forms, and then the plant begins to receive the benefit of the nitrogen assimilated by them. The life history of the nitrogen-assimilating bacteria appears parallel to that of the nitrifying organisms ; there is a period of multiplication with little assimilation, followed by a period in which nitrogen appears to be assimilated rapidly.

Variations in Inoculation Energy.

A study of the change in the power of soils to induce nitrification in a sterile soil was made at the same time as the determination of its rate of nitrification. The quantity of nitrates formed in three weeks in the sterilized soil kept under standard conditions has been taken as the measure of the inoculation energy of the soils.

The method used was as follows : Four jars of soil were kept under standard conditions, and nitrates determined in samples taken at the end of three, four, five, and six weeks, respectively. At the end of three weeks samples were used to inoculate a sterilized soil. At the end of four and five weeks similar sets were started. The amounts of nitrates formed in these soils in three weeks represents, therefore, the inoculation energy of the four jars of soil at different periods of time.

The inoculation energy of the soils increased rapidly with time. The results of the experiments are contained in Table II., which gives the total quantity of nitrates formed at the end of each period, as well as the inoculation energy of the soil measured as stated.

Table II.—*Variation of Inoculation Energy with Time.*

| | Milligrams nitrogen per kilogram soil. | | | | | |
| | Three weeks. | | Four weeks. | | Five weeks. | |
Nutrient.	In soil.	Inoculation energy.	In soil.	Inoculation energy.	In soil.	Inoculation energy.
Derived from 1748						
Jar 55 Cottonseed meal	52	81	193	141	202	205
" 56 Ammonium sulphate	15	4	63	57	...	219
" 57 Cottonseed meal	35	12	144	158	86	97
" 58 Ammonium sulphate	32	25	128	147	133	153
Derived from 1781						
Jar 91 Cottonseed meal	93	115	159	123		
" 92 " "	113	99	171	131		
" 93 Ammonium sulphate	75	60	124	75		
" 94 " "	24	75	138	139		

The broken curves in Fig. II. represent graphically the change in the inoculation energy of the soil with time. It might be expected that the inoculation energy of a soil would be related to its nitrification energy, but such does not seem to be the case, as may be readily seen by comparing the curves in Fig. I. with those in Fig. II. for the same soil.
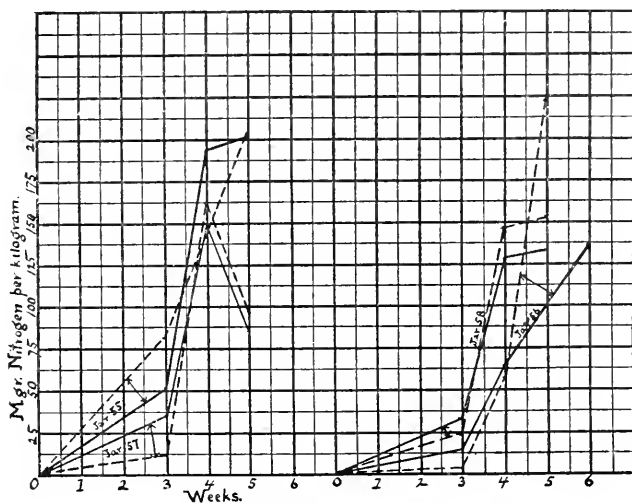
Fig. II.—Inoculation energy of soils (dotted lines) and total nitrification in same soils (solid lines). Arrows link corresponding curves.

There is, however, a close relation between the inoculation energy of the soil and the total quantity of nitrogen oxidized in it. Indeed, after the first three weeks, the inoculation energy of a soil seems to be as great as, or greater than, the total amount of nitrification in it. That is to say, after the first three weeks as much nitrification takes place in the inoculated soil in three weeks as takes place in the soil used for the inoculation in four or five weeks, as the case may be. The change in the power of the soil to induce nitrification is very great.

The relation between the total amount of nitrates formed in the soil and its inoculation energy is shown very clearly in Fig. II., in which the solid lines represent the total nitrification in the soil. Corresponding curves are linked by arrows. Even in the case in which denitrification took place (Jar 57), the inoculation energy of the soil is closely parallel to its total nitrification.

Causes of Variations in Inoculation Energy.

The changes in inoculation energy, as described above, are probably due to an increase in the number of the nitrifying bacteria in the soil. The increase does not seem to be attended with increased energy of nitrification, as has already been shown. That is to say, in the soils which have been studied, which are provided with an abundance of food and kept under favorable conditions, the number of the nitrifying organisms seems to increase throughout the course of the experiment while they nitrify slowly at first, then very rapidly, then very slowly again, in spite of the increase in their numbers.

It is possible that the increase observed in the inoculation energy of the soils is also due, in part, to an increased activity of the organisms, either that they multiply more rapidly in the inoculated soil or they grow in power to nitrify. A change of this kind would be analogous to the increase in activity or "virulence" observed with the bacteria which assimilate nitrogen.

Method of Work.

The following is the method of work followed throughout

this investigation. Two kinds of nitrification tests were made : In the direct nitrification tests, the soil was used as it came from the field ; in the inoculation tests, a sterilized soil was inoculated with active soils.

Direct Nitrification Experiments.—The soil was sifted through a 5 mm. sieve and 500 grams of it placed in a porcelain dish and mixed thoroughly with calcium carbonate, cottonseed meal or ammonium sulphate, and water. The mixture was transferred to a pint precipitating jar or fruit jar, weighed, and placed in a large water-bath in a dark closet, kept as nearly as possible at 35°. Every Monday and Thursday each jar was weighed and sufficient water added to restore its former weight. At the end of the period, usually three weeks, the proper amount of water was added to the jar, its contents mixed thoroughly in a porcelain dish, and the nitrates in 100 grams determined by the Tiemann-Schulze method. The remainder of the soil was allowed to nitrify further, if desired.

The amount of ammonium sulphate or cottonseed meal which was used for 500 grams soil contained 0.3 gram nitrogen. The ammonium sulphate was added in solution, after the calcium carbonate and water had been mixed with the soil. The calcium carbonate and cottonseed meal were always mixed thoroughly with the soil before any water was added. The calcium carbonate (2.14 grams) was just sufficient to neutralize all nitric and sulphuric acids which would be formed if all the ammonium sulphate were oxidized. In no case did this occur.

Water was used in quantity sufficient to bring the water content of the soil to one-third of its saturation capacity, allowing for the water already in the soil, and that to be added with the ammonium sulphate (20 cc.), if any. The method used to determine the water saturation capacity of the soils is as follows :

Fifty grams soil were placed on a porcelain plate in a carbon filter and the whole weighed. Water was added in quantity a little more than necessary to saturate the soil, so that a few drops came through, and the tube was allowed to drain, a

cork being placed loosely in it to prevent evaporation. After two hours, the stem of the tube was dried and the whole weighed. Allowance was made for water already in the soil.

Inoculation Experiments.—These differ from the preceding only in the use of a sterilized soil, and its inoculation with the soil to be tested. The same sterilized soil was used in all the inoculation experiments, being a sandy clay soil which had been in the laboratory, in a dry condition, for three years. No attempt was made to sterilize the soil completely, for sterilization as regards nitrifying organisms was all that was desired. A thorough drying is sufficient to accomplish this, but the soil used was also treated with chloroform, and then heated to a moderate temperature in an air-bath.

In case cottonseed meal was used, 20 grams of the soil to be tested were mixed with calcium carbonate and cottonseed meal, and then with 500 grams of the sterilized soil. Water was added in sufficient quantity (one-third of the soil's saturation capacity) and the whole thoroughly mixed. The nitrification was conducted as described above.

If ammonium sulphate was used, 20 grams of the soil were mixed with calcium carbonate and then with the sterilized soil. Water was added, and finally the ammonium sulphate in solution. This order was followed because it was not considered advisable to allow the ·strong solution of ammonium sulphate to come in direct contact with the germs in the inoculating soil.

It must be noted that the 100 grams of soil taken for the determination of nitrates did not represent one-fifth of the mixture, since the jar contained 500 grams of soil plus water, calcium carbonate, etc. Due allowance has been made for this fact where necessary.

Description of Soils.

1746. Sandy clay soil from a wheat field on the College farm. Little humus. Saturation capacity, 33 per cent.

1746*a*. A second sample, taken three weeks later.

1747. Sandy clay soil, sterilized as described previously. Used in all inoculation experiments. Saturation capacity, 34.3 per cent.

1748. Dark loam from peach orchard on the Experiment Station farm. Contains humus. Saturation capacity, 34 per cent.

1764. Black sandy soil from the Florida Experiment Station. It contained only 0.5 per cent of water when it arrived, and had little nitrifying power.

1764a. A second sample, which had been kept in a well-closed fruit jar since the summer of 1901. It was still quite moist.

1766. Loam from a flower bed on the College lawn. Contains much humus.

1766a. A second sample, taken three weeks later.

1768. A garden soil.

1772. Sandy soil from the test farm of the North Carolina Department of Agriculture, at Tarboro. Contained only 1.85 per cent water when received, but appeared moist. Saturation capacity, 27.3 per cent.

1779. Poor, light, sandy soil from the College farm. No humus. Saturation capacity, 27.3 per cent.

1779. Rich, dark, sandy soil from the College farm. Contains much humus. Saturation capacity, 46 per cent.

1781. Black sandy soil from the garden of the State Chemist, B. W. Kilgore. Contains much humus. Saturation capacity, 42.5 per cent.

Acknowledgment is hereby made to Chemist H. K. Miller, of Florida, and State Chemist B. W. Kilgore, of North Carolina, for kindness in furnishing samples of soil.

<div align="center">PART II.</div>

<div align="center">*The Nature of the Nitrifying Organisms.*</div>

In previous articles[1] from this Station by W. A. Withers and the author, the fact was brought out that some soils nitrify cottonseed meal to a greater extent than ammonium sulphate in three weeks, while with other soils the reverse is the case. The explanation advanced in the articles referred to for this circumstance is that the difference is due to the combined influence of three factors :

[1] J. Am. Chem. Soc., **23**, 318 (1901) ; **24**, 528 (1902).

1. Ammonium sulphate may hinder the action of the nitrifying organisms.

2. The acids produced by their life-activity are detrimental to them unless neutralized.

3. There are organisms which convert organic matter directly to nitrites or nitrates, as well as those which oxidize ammonium salts to nitrites.

According to this hypothesis, there are four groups of organisms which take part in the process of nitrification.

Group I. converts organic matter to ammonium salts.

Group II. converts ammonium salts to nitrites.

Group III. converts nitrites to nitrates.

Group IV. converts organic matter to nitrites or nitrates.

As stated, this hypothesis is based on the fact that some salts nitrify ammonium sulphate more readily than cottonseed meal, while other soils nitrify cottonseed meal more readily than ammonium sulphate. The work to be described in this section was designed to test this hypothesis more thoroughly.

The results of the work are as follows :

A. The difference in the ratio of nitrification of cottonseed meal and ammonium sulphate in different soils, is due to differences in the nitrifying organisms contained in those soils.

The following is the evidence in support of this statement :

1. A sterilized soil inoculated with different nitrifying soils nitrifies cottonseed meal and ammonium sulphate in different ratios. The only difference in the conditions of these experiments was the different soils used for the inoculation.

The figures are given in Table III.

Table III.—Relative Amounts of Cottonseed Meal and Ammonium Sulphate Nitrified in an Inoculated Soil.

	Soil.	Milligrams nitrogen per kilogram soil.		
		Cottonseed meal.	Ammonium sulphate.	Ratio.
1748	Loam	73	66	1 : 0.9
1746a	Sandy clay	100	53	1 : 0.5
1764a	Black sandy soil	99	61	1 : 0.6
1776a	Loam	29	7	1 : 0.3
1772	Sandy soil	23	10	1 : 0.4
1781	Black sandy soil	100	84	1 : 0.8

2. The ratio between the amounts of cottonseed meal and ammonium sulphate nitrified is nearly the same in any soil and in the inoculated soil prepared from it (Table IV.).

Table IV.—Relative Amounts of Cottonseed Meal and Ammonium Sulphate Nitrified in a Soil and in Its Inoculation.

	Soil.	Cottonseed meal.	Ammonium sulphate.	Ratio.
		Milligrams nitrogen per kilogram soil.		
1748	Direct	212	176	1 : 0.8
	Inoculation	73	66	1 : 0.9
1746a	Direct	176	77	1 : 0.45
	Inoculation	100	53	1 : 0.53
1772	Direct	5	3	1 : 0.6
	Inoculation	23	10	1 : 0.4
1781	Direct	284	267	1 : 0.9
	Inoculation	100	84	1 : 0.8

B. There are two groups of nitrifying organisms in the soil, one of which nitrifies cottonseed meal, the other ammonium sulphate. Besides the evidence afforded by the figures above given in support of this statement, it has been possible to increase the power of a soil to nitrify cottonseed meal, and to diminish it. If the nitrifying organisms are cultivated in a soil containing ammonium sulphate, and used to inoculate other soils, it will be found that their power of nitrifying cottonseed meal has diminished, and in the same way it is possible to increase the power of the soil to nitrify cottonseed meal by cultivation. The results of two sets of experiments of this kind are given in Table V.

Table V.—Effect of the Cultivation of the Organism on the Relative Amounts of Cottonseed Meal and Ammonium Sulphate Nitrified.

Set I. (1746)	Cottonseed meal.	Ammonium sulphate.	Ratio.
	Milligrams nitrogen per kilogram soil.		
Grown in cottonseed meal (mean)	233	162	1 : 0.7
" " ammonium sulphate	190	200	1 : 1.05
Set II. (1772)			
Grown in cottonseed meal	144	41	1 : 0.3
" " ammonium sulphate	116	64	1 : 0.6

An examination of the table shows that it is possible to in-

crease the relative numbers of either group of organisms by cultivation in the proper medium. That there are two groups of organisms of this kind is in itself no evidence that organisms exist which oxidize organic matter to nitrates or nitrites, however ; for we could assume that the germs which prepare cottonseed meal for nitrification by breaking it down to ammonium salts are diminished in relative number when the organisms are cultivated in a medium containing ammonium salts, and this assumption would, in part, explain the facts here given.

C. It seems probable that there are organisms which nitrify organic matter directly. If they do not exist, it should be possible to increase the rate of nitrification of ammonium salts without increasing the nitrification of cottonseed meal, but it should not be possible to increase the rate of nitrification of cottonseed meal without increasing that of ammonium sulphate, since the organisms which oxidize ammonium salts must increase in the same proportion as those which prepare the cottonseed meal by converting it into ammonium salts. If all the nitrification is effected by oxidation of ammonium salts as an intermediate stage, there should be more of these germs in a soil in which 233 milligrams nitrogen per kilogram are oxidized in the form of cottonseed meal, than where only 190 milligrams are so changed. But in the first case only 162 milligrams nitrogen in the form of ammonium sulphate are nitrified, in the second 200 milligrams. The fact that ammonium salts, in none of the cases mentioned in this article, are nitrified much faster than cottonseed meal, is also in favor of the view that organisms exist which can change organic matter directly to nitrates or nitrites. The only conclusive proof that can be offered is the isolation and study of an organism of this kind, which would not be an easy matter. At present the evidence is certainly in that direction.

PART III.

Determination of the Comparative Nitrifying Power of Soils.

The work recorded in this article serves as a basis for a method of determining the relative nitrifying power of soils,

which it is believed will lead to very important results. The nitrifying properties of soils may be studied with regard to several points:

1. *Number of Germs in the Soil.*—As has been shown in this article, the number of nitrifying organisms in any given soil is subject to wide fluctuations. As the activity of the germs varies as well as their number, it may be said that at present there is no method for comparing the relative number of germs in different soils.

2. *Nature of Germs.*—It is not considered of practical importance to determine the relative numbers of germs in soils which nitrify organic matter, and which nitrify ammonium salts, since it is probable that both groups of organisms are present in every soil, and their numbers may be increased by proper treatment.

3. *Comparative Nitrifying Power of Soils.*—This regards the soil only as a medium for the growth of the nitrifying organisms, and has for its object the comparison of the capacity of different soils to support nitrifying organisms.

In order to compare the nitrifying power of two or more soils, it is necessary that they should be placed under conditions favorable for nitrification, the conditions being exactly alike for each soil, and each soil should contain exactly the same number of nitrifying organisms with the same activity.

Method of Work.

The soils to be tested are sterilized by drying and treatment with chloroform, and are heated again to drive off the chloroform. Inoculation tests are then instituted on the soils as described in the earlier part of this paper. All the soils to be compared should be inoculated at the same time and with the same soil. For a number of soils, a standard soil can be used for comparison. At the end of three weeks, the quantity of nitrates in each soil is a measure of its ability to support the nitrifying organisms under the conditions of the experiment. In many cases it will be found of value to determine the nitrates at the end of the fourth, or even the fifth, week, especially if the soil used for the inoculation has a low inoculation in-

tensity. Where a number of soils are to be studied it would be of advantage to prepare a soil for inoculation with a high inoculation intensity.

Table VI. shows the application of this method to the determination of the relative nitrifying power of three soils.

Table VI.—Relative Nitrifying Power of Soils.

Nutrient.	Milligrams nitrogen per kilogram soil.		
	Poor sandy soil.	Rich sandy soil.	Sandy clay soil.
Cottonseed meal	2	116	..
Ammonium sulphate	3	73	77

The figures are the mean of duplicates. It is seen that the poor sandy soil has little power of nitrification for either ammonium sulphate or cottonseed meal. The nitrifying powers of the soils for cottonseed meal are in the proportion 1 : 58, and for ammonium sulphate, 1 : 24 : 25.

Application of the Method.

As seen above, different soils have very different capacity to support the nitrifying organisms. It is not known clearly why this is so, and how cultivation and treatment of the soil may modify its nitrifying powers. There is a great field for the study of the comparative nitrifying powers of soils in connection with the soil survey going on in the different states. By comparing the nitrifying powers of the different typical soils, it should be possible to divide them into different groups, according to their ability to support the nitrifying bacteria. This classification having been made, it can serve as a basis on which to determine the different factors which influence nitrification in the different typical soils. It will then become possible to control this very important process of nitrification in the field, at least to a large extent.

It is believed that this is a very important field for research, one in which the results will have a bearing of great importance for practical agriculture, and for agricultural chemistry.

Summary.

1. The number of nitrifying organisms in a given soil varies according to the conditions to which the soil is exposed.

2. The activity of the organisms is periodic. There is a period of rapid nitrification, preceded and followed by periods of comparative inactivity.

3. The inoculation intensity of a soil provided with nitrogenous matter, meaning its power to induce nitrification in a sterilized soil, increased with the time during the whole course of the experiments.

4. The nitrifying bacteria probably multiply continuously during such an experiment, and there are periods in which they nitrify very little.

5. It is possible to increase the inoculating power of a soil greatly.

6. The difference in the rate of nitrification of cottonseed meal and of ammonium sulphate in different soils is due to a difference in the organisms in the soils, since the same differences appear in the same sterilized soil inoculated with different nitrifying soils.

7. There are two groups of nitrifying organisms in soils, one of which nitrifies cottonseed meal more readily and the other ammonium sulphate. It is possible to increase the relative numbers of one or the other group by growing them in a soil containing cottonseed meal or ammonium sulphate.

8. Four groups of organisms take part in nitrification : those which convert organic matter to ammonium salts, those which convert ammonium salts to nitrites, those which convert nitrites to nitrates, and those which convert organic matter to nitrites or nitrates.

9. In order to compare the relative value of the medium which different soils offer for the growth of nitrifying organisms, the soils to be compared must be kept under the same conditions, and each soil must contain the same number of nitrifying organisms, of the same degree of activity.

10. A method is described for determining the comparative nitrifying powers of soils.

11. It is believed that the study of the comparative nitrifying powers of soils in connection with different soil types will be of great value as serving as a basis for the study of the different factors which influence nitrification in the different types of soils.

A SUGGESTED EXPLANATION OF THE REDUCTION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.

By J. C. Olsen.

The reduction of permanganic acid by manganese peroxide with the evolution of oxygen was discovered by Morse and studied by Hopkins and Walker, working under his direction.[1] He suggested, as an explanation of this, that the manganese peroxide might have the power of polymerizing, and, to satisfy this tendency, might take molecules of manganese peroxide from permanganic acid molecules, thus liberating oxygen.[2] Morse and Byers studied the phenomenon very thoroughly and found many facts which confirm the hypothesis of Morse and Reese.[3] The decomposition does not take place to any marked extent except in acid solution. The action was studied in solutions acidified with nitric and sulphuric acids, respectively, and the surprising fact was noted that, in the presence of nitric acid, the permanganate is decomposed about three times as rapidly as in the presence of an equivalent amount of sulphuric acid. Morse and Byers were unable to suggest any explanation of why this ratio was not identical with that of the relative strengths of the two acids.

One of us and Morse studied this phenomenon for a short time in the laboratory of the Johns Hopkins University. The records of this investigation were lost in a fire that partially destroyed the laboratory. The experiments were repeated by one of us. A carefully standardized solution of potassium permanganate, containing 40 grams of the salt to the liter, was prepared, as well as $\frac{2}{5}$-normal solutions of sulphuric and nitric acids. Glass stoppers were ground into oil sample-bottles of about 125 cc. capacity. It was found that the stoppers could be made gas-tight by wire fasteners. Twenty cc. of the

[1] Morse, Hopkins, and Walker : This Journal, 18, 401.

[2] Morse and Reese : *Ibid.*, 20, 721.

[3] Morse and Byers : *Ibid.*, 23, 313.

permanganate solution were introduced into each bottle with enough standard oxalic acid to reduce one-quarter of the permanganate, and sufficient sulphuric or nitric acid to liberate all of the permanganic acid and leave an excess of 1.5 molecules of monovalent acid for each molecule of undecomposed permanganic acid. The total volume was then made up to 60 cc. Solutions were prepared in which all of the acid was respectively sulphuric and nitric. Other bottles were filled with solutions in which half of the acid was sulphuric and half nitric. Still others were prepared in which 5 and 10 per cent, respectively, of the total acid was sulphuric, the remainder being nitric acid. The bottles were then placed in a thermostat maintained at 35° C. and were fastened to a horizontal shaft which made from 35 to 40 revolutions per minute. The rotation caused the manganese peroxide to drop through the solution twice each revolution. This method of agitation had been found by Morse and Byers to be the most favorable one for the action of the manganese peroxide on the permanganate. After seventy-two hours' agitation, the bottles were opened and the available oxygen remaining in the permanganate and manganese peroxide was determined by means of standard oxalic acid. The results of one of these experiments are given in tabular form below :

Table I.

Volume of $KMnO_4$. cc.	Volume of $KMnO_4$ reduced to MnO_2. cc.	Per cent of total acid. H_2SO_4.	HNO_3.	Volume of $KMnO_4$ decomposed by MnO_2. cc.	Average. cc.	Ratio of $KMnO_4$ decomposed.
15	5		100	4.13		
15	5		100	4.33	4.23	3.81
15	5	5	95	2.56		
15	5	5	95	2.69	2.62	2.36
15	5	10	90	2.03		
15	5	10	90	2.15	2.09	1.88
15	5	20	80	1.83		
15	5	20	80	1.84	1.84	1.66
15	5	30	70	1.71		
15	5	30	70	1.69	1.70	1.53
15	5	50	50	1.45	1.48	
15	5	50	50	1.51		1.33
15	5	100		1.10		
15	5	100		1.12	1.11	1.00

Inspection of these results shows that the influence of each acid, when both are present in the same solution, can by no means be calculated from the amount of decomposition produced by each acid when acting alone. When half of the acid present is sulphuric and half nitric, the decomposition is much less than a mean between the amounts of decomposition produced by each acid alone. Even 5 per cent of sulphuric acid reduces the decomposition to 62 per cent of the amount when only nitric acid is present. An explanation of this phenomenon was at first sought by a study of the conditions existing in the permanganate solution.

When both nitric and sulphuric acids were present, the solution contained, besides these acids, their potassium salts, free permanganic acid and potassium permanganate, the ions of these acids, and the potassium ion. It is a well-known fact that the strength of an acid is reduced by the presence of its salts. Calculations based on the dissociation theory and the known concentration of the various salts and acids in the solutions used seemed to show that sulphuric acid would be weakened by the presence of potassium sulphate much more than the nitric acid would be weakened by the presence of potassium nitrate. The calculated decomposition for the solution containing 50 per cent of each acid agreed quite well with that found by experiment. The results of the calculation for the solutions containing 5 and 10 per cent of sulphuric acid did not agree with the experimental results. It was also thought that the potassium might influence the reaction because of its well-known property of combining with the manganese peroxide.

It was therefore thought desirable to carry on the experiments with permanganic acid free from potassium. For this purpose the electrolytic method of preparing permanganic acid was devised.[1] One of us carried out experiments on permanganic acid prepared in this manner and which was free from potassium. The solutions were prepared and shaken in a manner identical with that of the series in which potassium permanganate was used, except that the amount of sulphuric

[1] This JOURNAL, **23**, 5, 431.

acid or nitric acid used was less by the amount necessary to neutralize the potassium of the permanganate. The amount of permanganic acid used was equal to that calculated to be equivalent in oxidizing power to 0.800 gram of potassium permanganate. The results are given in the following table:

Table II.

$HMnO_4$. Gram.	$HMnO_4$ reduced to MnO_2. Gram.	Per cent of total acid. H_2SO_4.	HNO_3.	Volume of 4 per cent. $HMnO_4$ decomposed by MnO_2. cc.	Average. cc.	Ratio of $HMnO_4$ decomposed.
0.607	0.152	100		1.34		
0.607	0.152	100		1.34		
0.607	0.152	100		1.43		
0.607	0.152	100		1.40		
0.607	0.152	100		1.28		
0.607	0.152	100		1.32	1.35	1.00
0.607	0.152	50	50	1.41		
0.607	0.152	50	50	1.43	1.42	1.05
0.607	0.152	5	95	1.92		
0.607	0.152	5	95	2.22	2.07	1.53
0.607	0.152		100	3.28		
0.607	0.152		100	3.59		
0.607	0.153		100	3.19		
0.607	0.152		100	3.18		
0.607	0.152		100	3.32		
0.607	0.152		100	3.40	3.33	2.47

These results are the same in general character as those obtained with potassium permanganate. Although the decomposition in the presence of nitric acid alone is relatively not so great as when potassium is present, the peculiar feature remains that 5 per cent of sulphuric acid is able to cause the decomposition to fall from 3.33 cc. to 2.07 cc., while, when the nitric acid is entirely replaced by the sulphuric acid, the amount of decomposition falls only from 2.07 cc. to 1.35 cc. The curves obtained by plotting each set of results are almost identical. As the only condition which had been changed was the removal of the potassium from the solution, it is fair to assume that this element is not the cause of this peculiarity of the decomposition.

FURTHER STUDY OF THE DECOMPOSITION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.[1]

BY J. C. OLSEN AND F. S. WHITE.

Having failed to find by a study of the solution an explanation of the marked retardation of the rate of decomposition of permanganic acid by manganese peroxide produced by even small quantities of sulphuric acid, the manganese peroxide precipitated under the various conditions involved was investigated. It was first noticed that when manganese peroxide is precipitated by oxalic acid from a solution containing sulphuric acid, it retains, with some persistence, part of the sulphuric acid, while the oxide precipitated from solutions containing nitric acid does not retain a trace of that acid. If both acids are present in the solution, the precipitated manganese peroxide will retain the sulphuric acid only. In each case the precipitate was filtered off on asbestos and washed until the wash-water no longer showed the color of permanganic acid. It was found that the sulphuric acid held by the precipitate could be completely removed by persistent washing with distilled water, about three times as much water being required for this purpose as was necessary to remove the permanganate. A blank test was made in which a solution containing as much sulphuric acid as was used with the permanganate was filtered through asbestos, which was then washed with as much water as had been found necessary to remove the permanganate from the manganese peroxide. The asbestos was then found to be free from sulphuric acid. It would seem, therefore, that, under the conditions studied, sulphuric acid forms a chemical compound with manganese peroxide which is easily dissociated by water, while nitric acid does not form a similar compound.

The frequently observed and striking phenomenon that, when manganese peroxide is dissolved by oxalic acid, the well-known permanganate color is developed for an instant, suggested the idea that manganese peroxide might also enter into chemical combination with permanganic acid. Such a

[1] This work was done in the chemical laboratory of the Polytechnic Institute of Brooklyn.

salt would probably be very unstable, decomposing with evolution of oxygen and the formation of a polymerized manganese peroxide. Morse and Byers[1] have already proved that the oxide remaining after a solution of permanganate had been acted on by manganese peroxide is such a polymerized oxide. If sulphuric acid is present, however, part of the manganese peroxide will combine with it instead of with the permanganic acid. The evolution of oxygen will, therefore, be slow. If only nitric acid is present, all of the manganese peroxide will be free to combine with the permanganic acid, and thus the evolution of oxygen will be rapid. All of the observed phenomena of the reduction of permanganate solutions by means of manganese peroxide can, therefore, be explained by the weak basic properties of manganese peroxide and a tendency to unite with sulphuric acid rather than with the nitric or permanganic acids. The existence of compounds of manganese with chlorine and fluorine, in which the manganese acts as a tetravalent base, has long been recognized.

To test the correctness of this theory, determinations were made of the amount of sulphuric acid held by the manganese peroxide precipitated under the same conditions as when the amount of oxygen evolved was determined. The amount of available oxygen in the manganese peroxide was also determined, since, if the permanganate solution was decomposed by the union of permanganic acid with the manganese peroxide, the latter ought to show, on analysis, a larger per cent of oxygen than the theoretical for MnO_2.

The determinations of sulphuric acid were made as follows : A solution was made containing 0.800 gram of potassium permanganate, and sufficient acid to neutralize all of the potassium and leave 1.5 molecules of free acid for each molecule of permanganic acid. One-fourth of the permanganate was reduced to manganese peroxide by standard oxalic acid and the volume of the solution made up to 60 cc. After standing over night the precipitate was filtered off on asbestos and washed free from permanganate with 50 cc. of water ; then further washing with about 150 cc. freed the precipitate from

sulphuric acid, which was precipitated by barium chloride and weighed on a Gooch crucible. As the results were not very concordant, another method of determining the sulphuric acid was adopted. The washings were transferred to a weighed platinum dish, neutralized with freshly distilled ammonia, evaporated to dryness, and brought to constant weight by drying at 110° C. The ammonium sulphate was then volatilized by gently heating the platinum dish, which was again weighed. The residue in the dish was then washed with water and the dish again weighed. In this manner the amount of free sulphuric acid could be calculated from the weight of ammonium sulphate. The amount of sulphuric acid combined as potassium sulphate was found from the loss in weight on washing the residue with water, while a slight amount of manganese peroxide generally remained which was probably present in the solution as manganous sulphate. The results of these experiments are given in the following tables :

Table III.

Per cent of total acid.		Weight of $BaSO_4$ found.	Equivalent of $BaSO_4$ in H_2SO_4.	
H_2SO_4.	HNO_3.	Gram.	Gram.	cc. of $^2/_5 N$ acid.
100		0.0056	0.0023	0.12
100		0.0073	0.0030	0.16
100		0.0091	0.0038	0.20
100		0.0109	0.0046	0.24
100		0.0137	0.0058	0.31
100		0.0133	0.0056	0.30
50	50	0.0200	0.0084	0.45
50	50	0.0198	0.0083	0.44

Table IV.

Per cent of total acid.		Free H_2SO_4 found.		H_2SO_4 as K_2SO_4.	
H_2SO_4.	HNO_3.	$(NH_4)_2SO_4$. Gram.	H_2SO_4. Gram.	K_2SO_4. Gram.	H_2SO_4. Gram.
100		0.0055	0.0041	0.0050	0.0028
100		0.0053	0.0039	0.0025	0.0014
50	50	0.0066	0.0049	0.0051	0.0029
50	50	0.0061	0.0048	0.0069	0.0039
5	95	0.0023	0.0017	0.0010	0.0006
5	95	0.0021	0.0015	0.0020	0.0011

It will be noticed that when 50 per cent of the acid present in the solution is sulphuric, the manganese peroxide carries down rather more of this acid than when all of the acid is sulphuric, while when only 5 per cent of the total acid is sulphuric the amount carried down is still nearly half as much as when only sulphuric acid is present. The amount of sulphuric acid held by the precipitate is, therefore, approximately inversely proportional to the amount of oxygen evolved by it. This relation can be seen more clearly by reference to the accompanying curves.

The manganese peroxide which was analyzed for percentage of oxygen was made in the same manner as that which was washed to determine the amount of sulphuric acid held. It was allowed to stand over night in contact with the solution without shaking. It was then filtered off on asbestos and washed free from permanganate. The asbestos, with the precipitate, was transferred to a beaker and treated with an excess of standard oxalic acid solution and sulphuric acid. When the manganese peroxide was dissolved, the excess of oxalic acid was titrated with standard potassium permanganate solution. In this manner the amount of available oxygen was determined. The excess of sulphuric acid was neutralized by shaking the solution with zinc oxide, and the total manganese determined by the Volhard method. By deducting the amount of manganese contained in the standard potassium permanganate which had been added, the amount of manganese contained in the manganese peroxide was obtained. The results obtained by this method were not very concordant. Analysis of manganese peroxide made by the Volhard method gave results above the theoretical for MnO_2.

	Calculated for MnO_2.	Found. I.	II.
O	36.78	37.39	37.36

Another method of analysis was therefore adopted. The available oxygen was obtained by dissolving the manganese peroxide in dilute hydrochloric acid and potassium iodide, the asbestos with the precipitate being transferred to a glass-stoppered bottle, adding an excess of 10 per cent potassium iodide and dilute hydrochloric acid, and allowing the whole to

stand in the cold until the precipitate was completely dissolved. The iodine liberated was then determined by means of standard thiosulphate solution. The solution was then transferred to a platinum dish, an excess of sodium phosphate added, brought to a boil, and cautiously neutralized with recently distilled ammonia. By stirring and slowly adding ammonia, the manganese was precipitated as the crystalline ammonium manganese phosphate. It was ignited and weighed as manganese pyrophosphate. This method gave more concordant results, manganese peroxide made by the Volhard method giving 36.81 per cent of oxygen instead of the theoretical 36.78 per cent. The results of these analyses are given in the two following tables, the first giving the results of the analysis by oxalic acid and the Volhard method, the second giving the results obtained by the iodine and pyrophosphate method :

Table V.—Analysis of Manganese Peroxide by Oxalic Acid and the Volhard Method.

Per cent of total acid.		Per cent of oxygen.
H_2SO_4.	HNO_3.	
	100	37.83
	100	37.88
50	50	37.16
50	50	37.05
50	50	37.00
100		36.66
100		36.47
100		36.79
100		36.87
100		36.98

Table VI.—Analysis of Manganese Peroxide by the Iodometric Method and Precipitation of Manganese as Phosphate.

Per cent of total acid.		Per cent of oxygen.
H_2SO_4.	HNO_3.	
	100	38.60
	100	38.91
5	95	38.36
5	95	37.46
50	50	37.80
50	50	36.56
100		36.80
100		37.44

Inspection of this table shows that the highest amount of oxygen found (38.91 per cent) was obtained in the analysis of a precipitate made in the presence of nitric acid, while the lowest (36.47 per cent) was obtained in the analysis of a precipitate made in the presence of sulphuric acid, while when both acids were present the values ranged between these extremes. Considerable variations will be noticed in analyses of precipitates made in apparently the same manner. It must be remembered, however, that the oxygen is held very closely, and is, no doubt, being given off during the manipulation of the precipitate. This instability is well shown by the analysis of the manganese peroxide which has been shaken with the permanganate solution. Under these conditions the oxygen is evolved quite regularly and the precipitate contains approximately the theoretical amount of oxygen for manganese peroxide. These results are given in the following table :

Table VII.—Analysis of Manganese Peroxide which Had Been Shaken with Acid Permanganate Solution.

Per cent of total acid.		Per cent of oxygen.
H_2SO_4.	HNO_3.	
	100	36.79
	100	36.76
5	95	37.22
5	95	36.95
5	95	37.36
5	95	37.00
10	90	36.00
10	90	36.80
50	50	37.11
50	50	37.16
100		37.09
100		36.90

For ease of comparison, the experimental results given in this paper have been plotted as curves. The abscissas of all the curves represent percentages of nitric acid and sulphuric acid in the solution from which the manganese peroxide was precipitated. Curve (1) represents the amount of oxygen evolved from solutions of potassium permanganate. Curve (2) represents the amount of oxygen evolved from solutions of permanganic acid, the conditions being identical with those
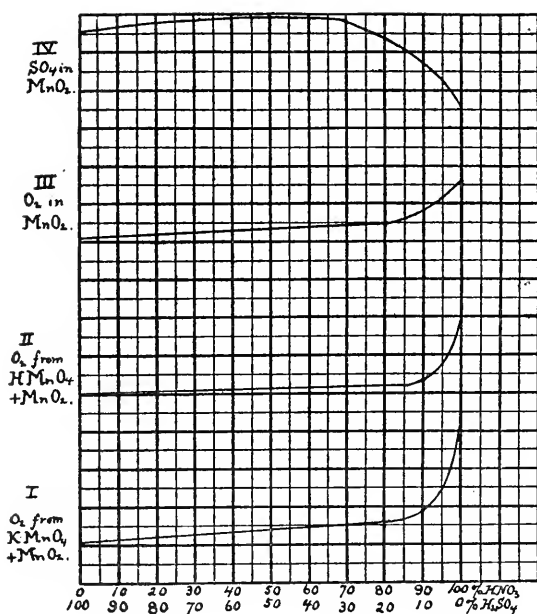
of curve (1). The similarity of these curves proves that the peculiarities of the decomposition of the permanganate in the presence of nitric and sulphuric acids is not due to the presence of the potassium. The experimental data of curve (1) are given in Table I., while those of curve (2) are given in Table II. Curve (3) gives the amount of oxygen contained in the manganese peroxide above the theoretical value for manganese peroxide. The experimental data are given in Tables V. and VI. The amount of oxygen held by the precipitate under some conditions seems to be proportional to the amount of oxygen given off from the solution when the conditions favor its evolution. Curve (4) represents the amount of sulphuric acid held by the manganese peroxide. Tables III. and IV. give the experimental data. The amount of sulphuric acid held by the manganese peroxide seems to be inversely proportional to the amount of oxygen held. It seems reasonable to suppose that in this reaction the manganese peroxide acts as a base and combines either with sul-

phuric or permanganic acid. The permanganic permanganate being unstable readily decomposes with evolution of oxygen and the formation of a polymerized manganese peroxide, which is a very much less active compound than the original manganese peroxide. We expect to continue this investigation and hope to get more direct evidence for the existence of a compound of manganese peroxide and permanganic acid.

ON THE OXIMES OF NITROMALONIC ALDEHYDE.[1]

By Henry B. Hill and William J. Hale.

In studying the action of hydroxylamine upon nitromalonic aldehyde, Hill and Torrey[2] found that the salts of the nitromalonic dialdoxime could readily be isolated, but, as was to be expected, that the β-nitroisoxazol was the only product which could be obtained under conditions favorable to the formation of the corresponding monoxime. They also found that a complicated reaction ensued when the dialdoxime was liberated by the addition of acid to the aqueous solution of its salts, but they were unable at the time to make a more careful study of the products which were thus formed. We have now made a further investigation of the oximes of nitromalonic aldehyde, and although this study is not yet completed, we think it best to publish the results which we have obtained as we are unable to continue the work together.

We have not succeeded in isolating the nitromalonic dialdoxime, but have found that it is completely decomposed at ordinary temperatures in dilute aqueous solution in the course of a few hours. The most important product of this spontaneous decomposition is fulminuric acid, and its formation shows that the dialdoxime must have retained both of its oxime groups under these conditions. At the same time it affords an interesting confirmation of the formula for fulminuric acid,

---

[1] A part of the work described in the following paper formed a portion of a thesis presented to the Faculty of Arts and Sciences of Harvard University in May, 1902, by William J. Hale, candidate for the degree of Doctor of Philosophy.

[2] This Journal, **22**, 89 (1899).

which was suggested by Steiner[1] and afterwards supported by Nef.[2]

$$CH=N—OH$$
$$|$$
$$C=N{\stackrel{O}{<}}_{OH}$$
$$|$$
$$CH=N—OH$$

→

$$CN$$
$$|$$
$$C=N{\stackrel{O}{<}}_{OH}$$
$$|$$
$$CO—NH_2$$
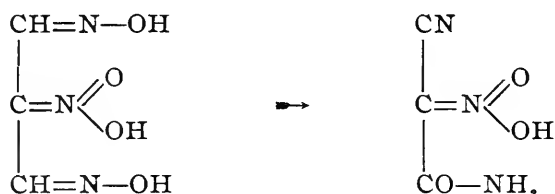
As a secondary product of the reaction there is formed in small quantity a crystalline body isomeric with fulminuric acid. We were unable to study it in detail until we found that it could readily be made from the nitromalonic aldoxime nitril or its acetyl derivative, and we shall discuss it more at length in connection with these bodies. Under certain conditions the dialdoxime may also lose a molecule of hydroxylamine, and β-nitroisoxazol is then formed. When a salt of the dioxime is decomposed by the addition of hydrochloric acid, a brilliant, yellow, crystalline body is at first thrown down, but this is so unstable that we have been unable to determine its nature. It may possibly be one form of the dialdoxime which is rapidly isomerized to a more stable configuration.

By the action of acetic anhydride upon the sodium salt of the dialdoxime in alkaline solution, the corresponding diacetyl derivative can easily be made. It is acid in its character and forms well-defined salts. This diacetyl derivative or its alkaline salts, by the loss of 2 molecules of acetic acid, is converted into the nitromalonic aldoxime nitril, while the acetyl derivative of the latter appears as an intermediate product.

$$CH=N—O—CO—CH_3$$
$$|$$
$$C=N{\stackrel{O}{<}}_{OH}$$
$$|$$
$$CH=N—O—CO—CH_3$$

→

$$CN$$
$$|$$
$$C=N{\stackrel{O}{<}}_{OH}$$
$$|$$
$$CH=N—O—COCH_3$$

→
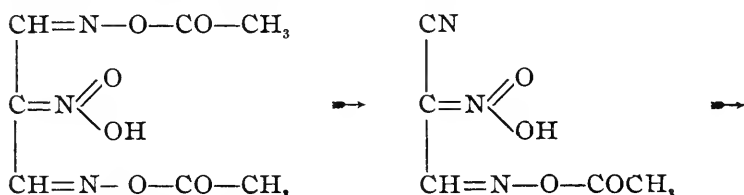
[1] Ber. d. chem. Ges., **9**, 784 (1876).
[2] Ann. Chem. (Liebig), **280**, 263 (1894).

$$
\begin{array}{l}
\text{CN} \\
| \\
\text{C}=\text{N} \diagup\!\!\!\diagdown \begin{array}{l} \text{O} \\ \text{OH} \end{array} \\
| \\
\text{CH}=\text{N}-\text{OH}
\end{array}
$$
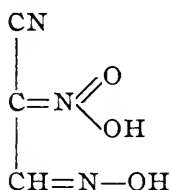
The nitromalonic aldoxime nitril is little affected by mineral acids, but it is converted into fulminuric acid by heating its alkaline solution. It forms two sets of salts, but the secondary salts are converted into the primary by the action of carbonic dioxide. If a solution of the secondary salt is acidified with 2 molecules of hydrochloric acid, a crystalline body gradually separates, which has the same composition as the aldoxime nitril, but which is identical in properties with the crystalline substance which is formed in small quantity by the spontaneous decomposition of the nitromalonic dialdoxime. With due care it may be recrystallized from hot water, but if the solution is not quickly cooled it is completely converted into fulminuric acid. By the action of a cold aqueous solution of potassic carbonate, or even of potassic acetate, potassic fulminurate is formed. When heated to 110° it gradually loses in weight, but decomposition soon sets in. We have as yet obtained no more definite evidence as to the structure of the body. Since it appears as an intermediate product between the aldoxime nitril and fulminuric acid, it evidently contains a cyanogen group, but its neutral character apparently excludes the possible presence either of an unaltered oxime or of an isonitro group. Its ready conversion into fulminuric acid is sufficient to show that the isonitro group has remained essentially unaltered, while the oxime group has already nearly completed its passage through the nitril to the amide. In the absence of further evidence, the formula

$$\begin{array}{c} CN \\ | \\ C=N \diagup{\!\!\!}^{O} \\ | \qquad\diagdown O \\ C \diagdown \\ | \qquad\diagdown OH \\ NH_2 \end{array}$$
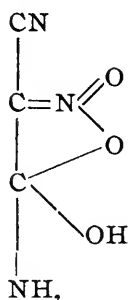
may be suggested as satisfying the conditions already named.

Since the nitromalonic aldoxime nitril is stable in acid solutions, we must conclude that it is isomerized in alkaline solution, as suggested in similar cases by Hantzsch,[1] and later by Abegg,[2] and that the oxime group passes from its *anti-* to its *syn*-form. While the salts of the *syn*-form are comparatively stable, the synoxime itself, when liberated, immediately enters into the reactions necessary to transform it into the amide, but at ordinary temperatures the change is arrested by the formation of the anhydride, and completed only by heat or the possibility of the formation of a salt of fulminuric acid.

Toward the end of our work we discovered that nitromalonic diacetyldialdoxime under certain conditions lost 2 molecules of acetic anhydride, with the formation of an acid wholly unlike the bodies previously obtained. While we were able to show by analyses of the stable, yellow silver salt that it was isomeric with fulminuric acid, we were unable to study it in detail, and a description of this product must therefore be postponed until the reaction can be more fully investigated.

Hill and Torrey[3] had already observed that aniline hydrochloride reacted upon the sodium salt of nitromalonic dialdoxime with the formation of the corresponding aldoxime anil melting at 162°,

[1] Ber. d. chem. Ges., **25**, 2164 (1892).
[2] *Ibid.*, **32**, 291 (1899).
[3] *Loc. cit.*, p. 108.

$$
\begin{array}{l}
\text{CH} = \text{N} - \text{OH} \\
\quad | \\
\text{C} = \text{N} \underset{\text{OH}}{\overset{\text{O}}{<}} \\
\quad | \\
\text{CH} = \text{NC}_6\text{H}_5
\end{array}
$$
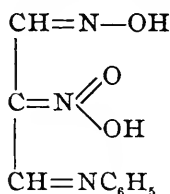
and that the same body could also be formed by the action of hydroxylamine upon the nitromalonic aldehyde anil described by them. If this aldoxime anil is heated for a long time with Beckmann's mixture, it loses a molecule of water and is converted into the corresponding nitril which melts at 208° (uncorr.) :

$$
\begin{array}{l}
\text{CN} \\
\quad | \\
\text{C} = \text{N} \underset{\text{OH}}{\overset{\text{O}}{<}} \\
\quad | \\
\text{CH} = \text{NC}_6\text{H}_5
\end{array}
$$
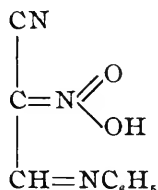
This nitril anil could also be made by the action of aniline hydrochloride upon an alkaline solution of the nitromalonic aldoxime nitril mentioned above, but it especially interested us in that we had already found that it was the chief product formed by the action of aniline upon an alcoholic solution of β-nitroisoxazol, a mode of formation which gave little clue to its structure. Since phenylhydrazine, under the same conditions, yields the 1-phenyl-4-nitropyrazol described by Hill and Torrey,[1] with the simultaneous formation of hydroxylamine, it may be assumed that in each case the isoxazol ring,

$$
\begin{array}{l}
\text{HC} = \text{N} \\
\quad | \qquad \searrow \text{O,} \\
\text{NO}_2\text{C} = \text{CH}
\end{array}
$$
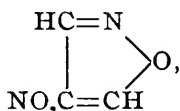
is opened by addition and the corresponding oximes,

[1] *Loc. cit.*, p. 104.

$$CH=N-OH$$
$$CN\diagup^{O}_{\diagdown OH}$$
$$CH=NC_6H_5$$

and

$$CH=N-OH$$
$$CN\diagup^{O}_{\diagdown OH}$$
$$CH=N-NH.C_6H_5$$

,
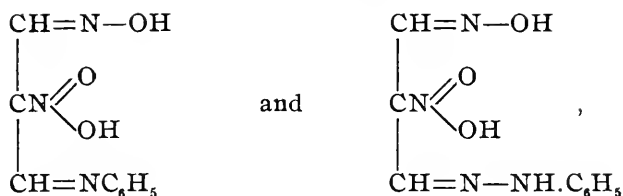
are at first formed. In the case of the aniline derivative the oxime then passes into the nitril by the loss of water, while the stable pyrazol ring is formed by preference from the hydrazone with the elimination of hydroxylamine.

When aniline hydrochloride reacts upon the sodium salt of the nitromalonic diacetyldialdoxime the acetyl derivative of the aldoxime anil,

$$CH=N-O-CO-CH_3$$
$$C=N\diagup^{O}_{\diagdown OH}$$
$$CH=NC_6H_5$$

,
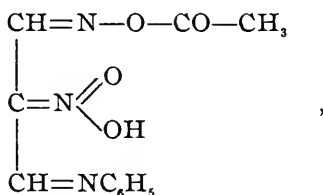
is formed with the simultaneous formation of hydroxylamine, and the same body may easily be made directly from the aldoxime anil by the action of acetic anhydride.

It had already been noticed that a cold aqueous solution of the β-nitroisoxazol soon turned yellow and acquired an acid reaction. We found that 1 molecule of sodic hydrate was apparently required to neutralize the acid which was ultimately formed, but at the same time the behavior of the solution toward aniline showed that no essential decomposition had taken place. On the addition of aniline acetate to the acid solution an abundant precipitate of the nitromalonic nitril anil was soon thrown down, while if sodic hydrate was added to alkaline reaction before the addition of the aniline salt, nitromalonic aldoxime anil was formed. The appearance of these two aniline derivatives,

$$\begin{array}{ccc}
\begin{array}{l}
\text{CN} \\
| \\
\text{C}{=}\text{N}\overset{\displaystyle O}{\underset{\displaystyle OH}{\Big\langle}} \\
| \\
\text{CH}{=}\text{NC}_6\text{H}_5
\end{array}
& \text{and} &
\begin{array}{l}
\text{CH}{=}\text{N—OH} \\
| \\
\text{C}{=}\text{N}\overset{\displaystyle O}{\underset{\displaystyle OH}{\Big\langle}} \\
| \\
\text{CH}{=}\text{NC}_6\text{H}_5
\end{array}
,
\end{array}$$
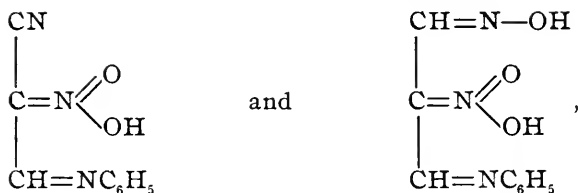
can be most readily explained by the assumption that the
β-nitroisoxazol takes up a molecule of water in dilute aqueous
solution and forms the monoxime of the nitromalonic alde-
hyde,

$$\begin{array}{l}
\text{CH}{=}\text{N—OH} \\
| \\
\text{C}{=}\text{N}\overset{\displaystyle O}{\underset{\displaystyle OH}{\Big\langle}} \\
| \\
\text{CH}{=}\text{O}
\end{array}.$$
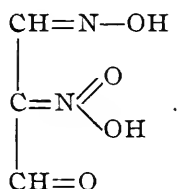
This body is necessarily acid in its character and should pass
readily into the anil by the action of aniline. That the un-
altered oxime group appears in the product when an aniline
salt is added in excess to an alkaline solution, while the cor-
responding nitril is formed from an acid solution, is, then, due
to the stability in alkaline or acid solution of different con-
figurations of the oxime. It must be noted, however, that
the direct formation of the synaldoxime from the β-nitroisoxa-
zol and its conversion into the antialdoxime in alkaline solu-
tion are not in accordance with the ordinarily accepted theo-
ries, and in apparent contradiction to the facts established in
the study of the nitromalonic aldoxime nitril.

If the aqueous solution of the β-nitroisoxazol is heated for
a short time it becomes bright yellow and strongly acid, as it
does on standing for a long time at ordinary temperatures, but
aniline now fails to show the presence of either form of the
monoxime of the nitromalonic aldehyde. Argentic nitrate,
however, throws down a bright-yellow, crystalline, silver salt
which has the formula $AgC_5HN_4O_4$, and the mother-liquor
contains formic acid in abundance. The simple reaction,

$$2C_3H_2N_2O_3 = C_5H_2N_4O_4 + CH_2O_2,$$
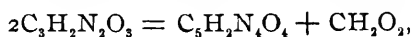
indicates that 2 molecules of the nitromalonic aldehyde mon-oxime which is first formed are condensed through one alde-hyde group, while the second is eliminated as formic acid, the two oxime groups that pass into cyanogen giving the body

$$
\begin{array}{c}
CN \\
| \\
C = N \diagup_{OH}^{O} \\
| \\
CH \\
\| \\
C - NO_2 \\
| \\
CN
\end{array}
$$
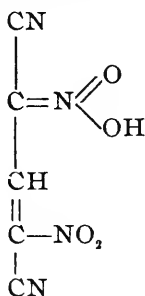
Although this formula explains satisfactorily the formation and the properties of the body, we have been able to find no additional evidence in confirmation of it.

Salts of Nitromalonic Dialdoxime.—When the sodium salt of nitromalonic aldehyde is dissolved in a concentrated solution of hydroxylamine hydrochloride, to which a slight excess of sodic carbonate has been added, a pale-yellow, sparingly soluble sodium salt of the corresponding dialdoxime soon separates which, as was shown by Hill and Torrey,[1] contains but a single atom of sodium. Since this salt dissolves readily in alkaline solutions, it seemed to us of interest to determine whether secondary or tertiary salts could not be isolated. The primary sodium salt was therefore suspended in cold water and carried into solution by the addition of 1 and 2 molecules of sodic hydrate. On the addition of alcohol to these solutions, yellow, crystalline salts were obtained which were dried *in vacuo* over sulphuric acid. Analyses of these products showed that they were both essentially the disodium salt, although that prepared with 1 molecule of sodic hydrate contained decidedly too small a percentage of sodium.

    I. 0.2156 gram salt gave 0.1552 gram Na_2SO_4.

    II. 0.1372 gram salt gave 0.1006 gram Na_2SO_4.

	Calculated for $Na_2C_3H_3N_3O_4$.	Found. I.	II.
Na	24.11	23.34	23.78

[1] *Loc. cit.*, p. 108.

On the addition of argentic nitrate to a solution of the di-
sodium salt, a voluminous, yellow precipitate was thrown
down, but it blackened rapidly on exposure to diffused day-
light, while the primary salt had previously been shown to be
extremely stable.

0.1840 gram salt gave 0.1471 gram AgCl.

	Calculated for $Ag_2C_3H_3N_3O_4$.	Found.
Ag	59.78	60.17

Nitromalonic Dialdoxime.—We have been unable to isolate
the nitromalonic dialdoxime from its salts, although we have
been able to prove that it exists for a short time in dilute
aqueous solution. When a slight excess of hydrochloric acid
is added to the sodium salt suspended in water, a bright-yel-
low, crystalline body is formed, which gradually disappears ;
if little water is used, the yellow crystals are replaced by col-
orless plates of the β-nitroisoxazol, or if more water is added,
the yellow body dissolves and ether then extracts the nitro-
isoxazol melting at 46° to 47°. When the sodium salt is sus-
pended in ether and 1 molecule of hydrochloric acid is added
with constant shaking, an ethereal solution is obtained which
throws down a yellow, crystalline precipitate on the addition
of ligroin, but in this case also the color soon fades and the
nitroisoxazol alone can be isolated. No more satisfactory re-
sults could be obtained by the addition of the requisite amount
of an ethereal solution of hydrochloric acid to the salt sus-
pended in ether. In each case the dioxime had evidently
been decomposed into β-nitroisoxazol and hydroxylamine ac-
cording to the equation

$$C_3H_5N_3O_4 = C_3H_2N_2O_3 + NH_2OH.$$
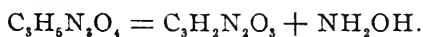
When exactly 1 molecule of hydrochloric acid was added in
dilute solution, the yellow body was thrown down and disap-
peared, and β-nitroisoxazol could be extracted with ether,
but the deep-red, aqueous solution gave reactions which
showed that it contained unaltered nitromalonic dialdoxime in
abundance. On the addition of aniline acetate a yellow, crys-
talline precipitate was soon formed which melted at 161°

to 162° after recrystallization from alcohol, and was in other respects identical with the nitromalonic aldoxime anil which Hill and Torrey had made by the action of aniline hydrochloride upon the sodium salt of the nitromalonic dialdoxime. When the solution was made alkaline with sodic hydrate, and was then shaken with acetic anhydride, the sodium salt of the nitromalonic diacetyldialdoxime, which we shall describe later, was immediately formed. The solution also gave with ferrous sulphate an intense red color, which became violet on the addition of sodic hydrate, color reactions which had already been mentioned by Hill and Torrey in their description of the nitromalonic dialdoxime. The deep-red solution of the dialdoxime gradually turned yellow on standing, and no longer gave any indication of the presence of the dioxime. In the course of twenty-four hours, slender, colorless needles were deposited, which were sparingly soluble in cold water and neutral in their reaction toward litmus. This body was formed in such small quantity that we were unable to study it in detail. We found that it was identical in composition with fulminuric acid, and that it could be converted into this acid by boiling it with water for a few minutes. Fortunately, we afterwards found that it could easily be made from the nitromalonic acetylaldoxime nitril, which we shall describe later, and a further account of it will be given in that connection. The strongly acid solution was neutralized with potassic carbonate and evaporated to a small volume. On cooling, fine, silky needles separated in abundance, which could easily be purified by recrystallization from hot water. As the silver salt proved to be sparingly soluble and could be crystallized from boiling water without decomposition, it was prepared and purified for analysis.

I. 0.2975 gram substance gave 0.2359 gram AgBr.

II. 0.2343 gram substance gave 0.1346 gram CO_2 and 0.0248 gram H_2O.

III. 0.2217 gram substance gave 34.2 cc. moist N at 18°.5 and 766 mm. pressure.

	Calculated for $AgC_3H_2N_3O_3$.	I.	Found. II.	III.
Ag	45.71	45.56	....	....
C	15.25	....	15.67	....
H	0.85	....	1.18	....
N	17.84	....	....	17.89

The composition of the salt and its physical properties warranted the conclusion that it was argentic fulminurate, and this conclusion was confirmed by the preparation of the characteristic cuprammonium salt, and by comparison with material obtained from mercuric fulminate. The acid itself was readily soluble in water or alcohol, very sparingly soluble in ether, and insoluble in chloroform, benzol, or ligroin. In a capillary tube it melted with decomposition at temperatures which varied from 136° to 149°, according to the rate of heating. The yield of potassic fulminurate was somewhat more than 30 per cent of the amount demanded by the equation

$$C_3H_5N_3O_4 = C_3H_3N_3O_3 + H_2O.$$

No other definite products of the reaction were isolated, but the behavior of the solution toward silver and copper salts showed that hydroxylamine had also been formed.

In order to assure ourselves that the conversion of the dialdoxime into fulminuric acid was not brought about by a slight accidental excess of hydrochloric acid, the well-washed silver salt was treated with pure hydrochloric acid, care being taken that a part of the silver salt remained unaltered. The filtered solution was found to be free from silver and hydrochloric acid, and gave an intense color reaction with ferrous sulphate. After standing for two hours at ordinary temperature the solution still turned slightly red, but at the end of three hours it gave absolutely no color with a ferrous salt. After the lapse of twenty-four hours a very slight crystalline precipitate had separated. The clear solution gave, with argentic nitrate, a yellowish, crystalline precipitate from which argentic fulminurate could be extracted with boiling water. No β-nitroisoxazol could be isolated with ether, but the ether left, on evaporation, a very small amount of a yellow oil which gave, with argentic nitrate, a yellow, microcrystalline precipitate. After thorough

extraction with ether the aqueous solution yielded long, colorless needles of argentic fulminurate on the addition of a crystal of argentic nitrate. On warming the solution from which the argentic fulminurate had been removed, with a drop of ammonic hydrate, metallic silver separated in abundance. In a solution absolutely free from hydrochloric acid the nitromalonic dialdoxime had therefore been partially converted into fulminuric acid, but at the same time a part of it had been decomposed with the formation of hydroxylamine.

Nitromalonic Diacetyldialdoxime.—When the sodium salt of nitromalonic dialdoxime is shaken in alkaline solution with acetic anhydride, the corresponding diacetyl derivative is immediately formed, and its sodium salt separates in the form of pale-yellow, finely felted needles. The salt may be purified by recrystallization from alcohol, and then forms small, obliquely truncated prisms.

I. 0.2486 gram salt gave 0.0702 gram Na_2SO_4.

II. 0.1798 gram salt gave 27.0 cc. moist N at $22°.2$ and 762 mm. pressure.

	Calculated for $C_7H_8N_3O_6Na$.	Found. I.	II.
Na	9.10	9.15	....
N	16.63	....	16.95

When quickly heated, the salt melts at $136°$ to $138°$ with decomposition and slight explosion, but when slowly heated it is decomposed at a lower temperature. It dissolves readily in warm water, but decomposition soon ensues with the formation of the acetylaldoxime nitril, which is described below. Various salts may be made from it by double decomposition, but none of them have been further examined. When warmed with 2 molecules of sodic or potassic hydrate a deep-red solution is obtained, which contains the alkaline salt of an acid isomeric with fulminuric acid. This reaction is now under investigation.

The ready decomposition in aqueous solution made it advisable to use absolute ether in the preparation of the free diacetyldialdoxime. The salt was therefore suspended in dry ether and an ethereal solution of hydrochloric acid added with

constant shaking. The ethereal solution was then evapora-
ted and the clustered needles thus obtained were recrystallized
from ether with the addition of a little ligroin. As the body
was found to lose acetic acid on standing for some time over
sulphuric acid, it was analyzed after it had been dried for a
few hours in a desiccator.

I. 0.1404 gram substance gave 0.1862 gram CO_2 and 0.0530
gram H_2O.

II. 0.1720 gram substance gave 28.6 cc. moist N at 23° and
757 mm. pressure.

	Calculated for $C_7H_9N_3O_6$.	I.	Found. II.
C	36.34	36.18	....
H	3.92	4.22	....
N	18.23	....	18.58

The nitromalonic dialdoxime crystallizes in globular aggre-
gations of fine, colorless needles which melt at 64° to 66°. It
dissolves readily in alcohol or chloroform, more sparingly in
ether or benzol, but it is nearly insoluble in ligroin or car-
bonic disulphide.

Nitromalonic Acetylaldoxime Nitril.—When the sodium salt
of nitromalonic diacetyldialdoxime is dissolved in water by
the aid of gentle heat, decomposition ensues and, on cooling,
crystals of the corresponding acetylaldoxime nitril are deposi-
ted, while the solution contains acetic acid. The same prod-
ucts result from the spontaneous decomposition of the diacetyl-
dialdoxime already mentioned. We have obtained the best
results by suspending the sodium salt in ten times its weight
of water and heating at 65° to 70° until complete solution is
effected. On cooling, nearly 60 per cent of the theoretical
amount of the new product may be obtained.

I. 0.1294 gram substance gave 0.1668 gram CO_2 and 0.0382
gram H_2O.

II. 0.0882 gram substance gave 18.9 cc. moist N at 17° and
764 mm. pressure.

	Calculated for $C_5H_5N_3O_4$.	I.	Found. II.
C	35.05	35.16	....
H	2.94	3.30	....
N	24.61	....	24.89

The nitromalonic acetylaldoxime nitril crystallizes in long, pointed prisms which melt at 87° to 88° (corr.). It is readily soluble in alcohol, ether, benzol, or chloroform ; sparingly soluble in carbonic disulphide, and still more sparingly soluble in ligroin. It may be most easily brought to its proper melting-point by recrystallization from ether. It dissolves freely in hot water, but at 100° acetic acid and nitromalonic aldoxime nitril are gradually formed. Even at 70° the same reaction slowly takes place, and in the method of preparation which we describe, the aldoxime nitril is found in the mother-liquors in considerable quantities. In alkaline solutions, salts of the aldoxime nitril are at once formed.

Nitromalonic Aldoxime Nitril.—The nitromalonic aldoxime nitril may easily be made by heating its acetyl derivative for some time at 100° with a small quantity of water. The reaction is much facilitated by the addition of a small amount of hydrochloric acid, and is then completed in the course of a few minutes. A part of the product separates as the solution cools and more may be obtained by concentration of the mother-liquor. The body was purified for analysis by recrystallization from hot water.

I. 0.1944 gram substance gave 0.1976 gram CO_2 and 0.0432 gram H_2O.

II. 0.0790 gram substance gave 22.6 cc. moist N at 20° and 761 mm. pressure.

	Calculated for $C_3H_3N_3O_3$.	Found. I.	II.
C	27.88	27.73	....
H	2.34	2.49	....
N	32.62	....	32.62

The nitromalonic aldoxime nitril crystallizes in long, colorless, dendritic needles, or from concentrated solutions in irregularly aggregated prisms, which melt at 143° to 144° (corr.). It is readily soluble in alcohol, ether, or hot water, sparingly soluble in cold water, chloroform, or benzol, and nearly insoluble in carbonic disulphide, or ligroin. It is but slowly attacked by mineral acids, but after heating for three hours in a sealed tube at 100° with concentrated hydrochloric

acid, it was found to be partially decomposed. The acid solution gave with silver and copper salts qualitative reactions for hydroxylamine. With acetic anhydride it readily forms the acetyl derivative which has just been described, but we have not yet been able to convert this acetyl derivative or the aldoxime itself into the corresponding nitromalonic nitril. The aldoxime dissolves promptly in solutions of the alkaline carbonates, and its salts may also conveniently be prepared by the action of caustic alkalies upon the acetyl derivative. In any case it was evident that two different salts could be made by varying the amount of the alkaline hydrate used. The sodium salts proved to be difficult of purification and we therefore prepared the dibarium salt for analysis, and from this the primary silver salt.

When the nitromalonic aldoxime or its acetyl derivative is dissolved in a cold saturated solution of baric hydrate, the dibarium salt gradually separates in pale-yellow, clustered needles. On heating, the salt turns a deeper yellow with the loss of water. Since the salt was decomposed by carbonic dioxide it was heated in a current of dry, purified air in order to determine the water of crystallization.

I. 0.2816 gram air-dried salt gave 0.2183 gram $BaSO_4$.

II. 0.2218 gram air-dried salt lost, at 155°, 0.0268 gram H_2O.

	Calculated for $C_3HN_3O_3Ba.2H_2O$.	I.	Found. II.
Ba	45.72	45.63	. . . .
H_2O	11.99	. . . .	12.09

This barium salt was suspended in water and decomposed with carbonic dioxide. On the addition of argentic nitrate to the filtered solution a pale-yellow, silver salt was thrown down in short, clustered needles, which proved, on analysis, to contain but 1 atom of silver.

0.1446 gram salt gave 0.1154 gram AgBr.

	Calculated for $AgC_3H_2N_3O_3$.	Found.
Ag	45.72	45.84

On the addition of aniline hydrochloride to an alkaline solution of the aldoxime nitril, the nitromalonic anil nitril, which

we shall soon describe, was at once formed. After one re-crystallization from glacial acetic acid it melted at 206° to 207° (uncorr.). When the aldoxime nitril is heated with an excess of potassic hydrate, fulminuric acid is soon formed.

If hydrochloric acid is added to a solution of a salt of the aldoxime nitril in precisely the amount required to liberate the oxime, the solution at first remains clear, but on standing it gradually deposits long, slender needles of a body isomeric with the aldoxime. The yield amounts to about 75 per cent of the weight of the oxime taken. The mother-liquor contains fulminuric acid, but no unaltered oxime could be detected. The body proved to be identical with the sparingly soluble product formed in small quantities by the spontaneous decomposition of the dialdoxime in aqueous solution. It is also formed, together with fulminuric acid, by the action of hydroxylamine upon β-nitroisoxazol. As we were unable to recrystallize the body without effecting a more or less complete isomerization, it was washed well with cold water and dried over sulphuric acid. The material obtained from the dialdoxime was barely sufficient for the analyses necessary to establish its composition.

I. 0.2126 gram substance gave 0.2174 gram CO_2 and 0.0526 gram H_2O.

II. 0.1162 gram substance gave 33.5 cc. moist N at 22° and 759 mm. pressure.

	Calculated for $C_3H_3N_3O_3$.	I.	Found. II.
C	27.88	27.90	. . . .
H	2.34	2.77	. . . .
N	32.62	. . . .	32.46

The body is very sparingly soluble in all ordinary organic solvents. It is also very sparingly soluble in cold water, but it dissolves freely on heating. If the hot solution is quickly cooled, a portion of the substance again separates in crystalline form, but if great care is not taken the body is completely converted into fulminuric acid and the solution remains clear on cooling. The body slowly dissolves in solutions of the alkaline carbonates with the formation of the corresponding

salts of fulminuric acid.   When triturated with concentrated solutions of potassic carbonate or potassic acetate, it soon gives, in the cold, the finely felted needles of potassic fulminurate.   In a capillary tube it melts with decomposition at from 128° to 140°, according to the rate of heating.   When heated at 110° it slowly loses in weight, but the loss in weight is evidently attended by decomposition.   As yet we have been unable to prepare from this body any derivatives which establish its structural relations to fulminuric acid.

Nitromalonic Acetylaldoxime Anil.—Hill and Torrey[1] have already described the product which is formed when aniline hydrochloride is added to a solution of the sodium salt of the nitromalonic dialdoxime.   One oxime group is eliminated in the form of hydroxylamine, and the crystalline nitromalonic aldoxime anil melting at 162° (uncorr.) is at at once thrown down.   They have also shown that the same body may be made by the action of hydroxylamine upon the nitromalonic aldehyde anil.   If this aldoxime anil is warmed with eight or ten times its weight of acetic anhydride, the acetyl derivative is soon formed.   As the solution cools, a part of the product separates in crystalline form, and the rest may be precipitated by dilution with water.   This same acetyl derivative may be prepared more conveniently by the action of aniline hydrochloride upon the sodium salt of the nitromalonic diacetyldialdoxime.   The product is somewhat viscous at first, but soon becomes crystalline, and the yield is over 80 per cent of the theoretical amount.   In this case hydroxylamine is formed and is readily isolated from the mother-liquor.   For its identification we added the hydrochloride to an alkaline solution of the nitromalonic aldehyde anil and obtained the aldoxime anil, which melted at 160° to 161° after one recrystallization from alcohol.

0.1802 gram substance gave 26.7 cc. moist N at 18° and 759 mm. pressure.

	Calculated for $C_{11}H_{11}N_3O_4$.	Found.
N	16.90	17.01

[1] *Loc. cit.*, p. 108.

The nitromalonic acetylaldoxime anil is readily soluble in alcohol, chloroform, benzol, or glacial acetic acid, less readily soluble in ether, and is sparingly soluble in carbonic disulphide or ligroin. It is insoluble in water, but is slowly decomposed by boiling water. From glacial acetic acid it crystallizes in yellow, radiating needles, or on slow cooling in well developed, obliquely truncated prisms. After repeated recrystallization from alcohol it melted at 114° to 115°, but crystallization from carbonic disulphide raised the melting-point to 115° to 116° (corr.). When gently warmed with dilute sodic hydrate it is immediately decomposed, and hydrochloric acid then precipitates the aldoxime anil melting at 162°.

Nitromalonic Nitril Anil.—The nitromalonic acetylaldoxime anil remains unchanged even after long heating with an excess of acetic anhydride, but with Beckmann's mixture it gradually passes into the nitril. The reaction is slow, and even after long boiling in a stream of gaseous hydrochloric acid but a small yield of the nitril is obtained. Still we had little difficulty in preparing in this way sufficient material to enable us to establish its identity. The excess of acetic acid was driven off on the water-bath, and the dark yellow crystals which separated on cooling were recrystallized from glacial acetic acid. The body then melted at 205° to 208° and was, in other respects, identical with material prepared by more convenient methods. The substance may be made most readily by the action of aniline upon an alcoholic solution of β-nitroisoxazol. If somewhat more than one molecule of aniline is added at ordinary temperatures, the nitril anil soon begins to separate, and in a short time the reaction is complete. The yellow crystalline precipitate is sparingly soluble in alcohol, and may be purified most conveniently by crystallization from glacial acetic acid or ethyl acetate.

I. 0.1843 gram substance gave 0.3866 gram CO_2 and 0.0767 gram H_2O.

II. 0.1642 gram substance gave 32.9 cc. moist N at 22°.5 and 758 mm. pressure.

	Calculated for $C_9H_7N_3O_2$.	I.	Found. II.
C	57.09	57.23	....
H	3.73	4.66	....
N	22.26	....	22.48

The nitromalonic nitril anil is insoluble in water and sparingly soluble in alcohol, ether, chloroform or benzol. It dissolves freely in hot glacial acetic acid, and, as the solution cools, it separates in compactly clustered, short, yellow prisms which melt at 208° (uncorr.). It dissolves quite readily in boiling ethyl acetate, and repeated recrystallization from this solvent gave the somewhat higher melting-point, 209° to 210° (uncorr.) or 215° to 216° (corr.). It dissolves promptly in cold dilute sodic hydrate and is reprecipitated unchanged on the addition of acids, but hot or concentrated sodic hydrate liberates aniline.

Reactions with Phenylhydrazine.—Phenylhydrazine was found to react upon β-nitroisoxazol in alcoholic solution with the evolution of heat, and as the solution cooled a somewhat dark-colored crystalline product separated. After recrystallization from alcohol, the substance melted at 126° to 127° (uncorr.) and proved to be identical in properties with the 1-phenyl-4-nitropyrazol described by Hill and Torrey[1] as formed from nitromalonic aldehyde by the action of phenylhydrazine. From the mother-liquors a white crystalline hydrochloride was obtained which gave, when heated with benzophenone, the corresponding oxime melting at 138° to 139°. The chief products of the reaction were, therefore, 1-phenyl-4-nitropyrazol and hydroxylamine. When phenylhydrazine hydrochloride is added to an aqueous solution of the sodium salt of the nitromalonic dialdoxime, an orange-red, viscous precipitate is thrown down which soon becomes crystalline ; on standing, the orange-red color soon passes into a dull brown. The crystalline product was dried and recrystallized from a mixture of ether and ligroin without the aid of heat. The melting-point, 126° to 127°, and other properties of the body showed that it was 1-phenyl-4-nitropyrazol. The orange-red needles which were formed at first were doubtless

[1] *Loc. cit.*, p. 104.

the unstable aldoxime hydrazone corresponding to the stable aldoxime anil which is formed under similar conditions by the action of aniline hydrochloride.

Action of Water upon β-Nitroisoxazol.—An aqueous solution of β-nitroisoxazol is at first apparently neutral to litmus, but it rapidly acquires an acid reaction and at the same time it turns bright yellow. We thought it of interest to determine, by titration, the amount of acid which was thus ultimately developed, although the rapid alteration of the nitroisoxazol in neutral solution made it impossible to determine by this method the percentage which remained unchanged in the acid solution at any given time. A decinormal solution of the nitroisoxazol was accordingly titrated with N/10 sodic hydrate after standing at ordinary temperatures for one, two, and three days. With phenolphthalein a satisfactory endpoint could be obtained, and in each case 1.004 molecules of sodic hydrate were required for 1 molecule of the nitroisoxazol. These figures made it probable that no more essential alteration of the nitroisoxazol had taken place than was involved in its conversion into the nitromalonic aldehyde aldoxime by the addition of a molecule of water, or in its direct isomerization into nitromalonic aldehyde nitril. Either product would require 1 molecule of sodic hydrate for its neutralization. An examination of the acid solution showed that it doubtless contained the aldehyde aldoxime. On extraction with ether β-nitroisoxazol could be recovered, which melted at 46° to 47°, after recrystallization from ether and ligroin. When aniline or aniline acetate was added directly to the acid solution, a crystalline precipitate of the nitromalonic nitril anil soon separated, which could easily be identified by its melting-point, 207° to 208°, and its other properties ; but if the solution was first made alkaline with sodic hydrate and an aniline salt then added in excess, nitromalonic aldoxime nitril melting at 161° to 162° was at once formed. As the solution stands, the yield of these two aniline derivatives diminishes from day to day, and the color of the precipitates obtained gradually becomes dark-brown instead of yellow. Finally the solution no longer reacts with aniline, but gives a flocculent

precipitate with argentic nitrate and gives qualitative tests for hydrocyanic and formic acids.

If β-nitroisoxazol is heated for a short time with water at 100°, a deep yellow, strongly acid solution is obtained, which does not react with aniline. If the solution is not heated too long, it gives, on the addition of argentic nitrate, beautiful long, yellow needles of a silver salt, which is sparingly soluble even in boiling water, but which may readily be recrystallized from very dilute nitric acid. The mother-liquors, on standing, gradually deposit a pale yellow, amorphous salt, which is apparently a mixture, but when boiled with dilute nitric acid it yields an additional quantity of the yellow crystalline salt (Analyses II and III). For analysis the salt was dried at 100° to 105°.

I. 0.1730 gram salt gave 0.1122 gram AgBr.

II. 0.1261 gram salt gave 0.0817 gram AgBr.

III. 0.1518 gram salt gave 0.0984 gram AgBr.

IV. 0.1662 gram salt gave 0.1256 gram CO_2 and 0.0106 gram H_2O.

V. 0.1722 gram salt gave 29.7 cc. moist N at 22°.2 and 759 mm. pressure.

VI. 0.1561 gram salt gave 27.2 cc. moist N at 23°.8 and 767 mm. pressure.

	Calculated for $AgC_5HN_4O_4$.	I.	II.	III.	Found. IV.	V.	VI.
Ag	37.33	37.27	37.22	37.25	....	...	....
C	20.75	....	....	....	20.62	....	....
H	0.35	....	....	....	0.71	....	....
N	19.43	....	....	....	....	19.40	19.65

The silver salt, when decomposed by dilute hydrochloric acid, gives a yellow acid solution which, on evaporation, or extraction with ether, yields a yellow, viscous syrup. From this viscous residue the crystalline silver salt may again be made without difficulty, but we have as yet been unable to prepare from it, or from the silver salt, other crystalline derivatives.

To the mother-liquor obtained in the preparation of the silver salt, sodic chloride was added until the whole of the silver

which it contained was precipitated, and the filtered solution was then distilled. The acid distillate contained formic acid in abundance, as was shown by qualitative test, and also by the analysis of the lead salt which was made from it by neutralization with plumbic carbonate.

0.2546 gram salt gave 0.2592 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	69.53

A METHOD FOR DETERMINING THE INDEX OF REFRACTION OF SOLID HYDROCARBONS WITH THE PULFRICH REFRAC- TOMETER.

INDEX OF REFRACTION OF THE SOLID HYDROCARBONS IN PETROLEUM.[1]

By Charles F. Mabery and Lee Shepherd.

One of the most important physical constants of liquids is the index of refraction from which the molecular refraction may be calculated. Of the two forms of apparatus in use for these determinations, the Abbé and Pulfrich refractometers, the latter is in all respects the most convenient. But neither refractometer as constructed permits of the determination of the index of solid bodies, which requires a rise in temperature sufficient to liquefy the solid. So far as we are aware, no method has been proposed for determining the index of solids. The only method suggested for ascertaining the index of liquids at increased temperatures is that of Brühl,[2] which depends on raising the temperature to the desired point by means of a copper bar of peculiar shape, extending to a sufficient distance from the prism to be heated by a lamp. Sufficient heat is applied to the bar to reach the desired temperature over the prism by conduction. A stirrer is also attached to insure equal heating of the liquid.

[2] Ber. d. chem. Ges., **24**, 286 (1891).

But this method is not satisfactory, especially for solids, since they require temperatures for melting that are difficult to maintain constant by external application without breaking the joint between the prism and the glass cup which holds the liquid. It occurred to us that a more convenient source of heat for melting solids might be supplied by means of an electric current passing through a wire of suitable size to afford the necessary resistance. After numerous experiments, that need not be described in detail, it was found that the heat from a coil of wire surrounding the glass cup containing the substance, even with a sheet of asbestos interposed, caused such unequal expansion of cup and prism that the lute cracked, causing leaks at the joint. On trying to maintain the desired temperature by a coil of wire placed within the glass cup it was found difficult to regulate the temperature at just the point desired. Finally it was found that a coil of wire surrounding the glass cup could be relied on to raise the temperature nearly to the point desired, and by means of an inner coil the temperature just required for melting could be obtained. German silver wire was found to be more suitable for the coils on account of its rigidity, and the size selected was No. 25 English standard gauge. The arrangement of outside and inside coils, prism, glass cup, and attachment for stirring the melted solid are shown in the figure.

The outer coil of wire *W*, is drawn over a thin sheet of asbestos *A*, which surrounds the glass cup, and another thicker sheet is placed outside to prevent radiation. German silver wire of the same size is used for the inner coil and connected above the glass cup to longer copper conductors, which are bent twice so as to dip into mercury cups. This coil is kept in place by means of a cork support *K*, and the asbestos cover *B*, which also serves to retain the heat. The inner coil also serves as a stirrer by moving it up and down, which is possible on account of the deep mercury cups. In this manner the solid, after melting, is very evenly heated. The solid is placed in the glass cup on the face of the prism *N*, melted by the heated wire, and the temperature kept constant by the inner coil, as indicated by the thermometer.
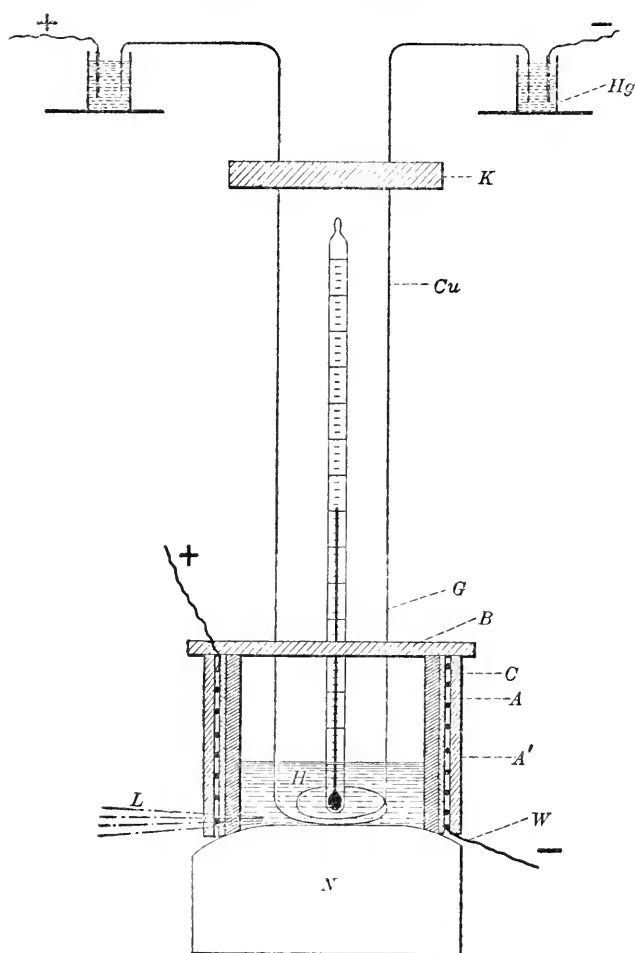
The rays of light L enter the prism through a slit in the asbestos, 0.5 cm. square. A current of 3 to 5 amperes was sufficient to maintain the temperatures desired in these determinations. With this combination of internal and external heating a temperature of 100° may readily be kept constant without fear of breaking the joint between the prism and glass cup.

The accuracy of this method of heating was determined with water with the following results :

	20°.	30°.	40°.	50°.	60°.	70°.
Angle	67°38′	67°51′	68°10′	68°10′	68°48′	70°9′
Index of refraction	1.3313	1.3304	1.3291	1.3276	1.3241	1.3208
Molecular refraction	3.692	3.692	3.692	3.692	3.691	3.692

Theoretical molecular refraction of water, 3.692.

This method was applied to the determination of the index of refraction of hydrocarbons separated from Pennsylvania petroleum direct, as described by one of us (Mabery) in a former paper,[1] and also to the same hydrocarbons separated from commercial paraffin. The bodies from crude petroleum had been distilled many times under a tension of 50 mm. and separated from the liquid hydrocarbons by cooling to a low temperature, pressing out the liquid hydrocarbon, and crystallization of the solids from ether and alcohol.

Attempts were first made to ascertain the index directly by melting the solid on the face of the prism, but on account of lack of uniformity in melting, a thin film of the solid persisted on the face of the prism and obstructed the passage of light. The method of mixture was, therefore, resorted to with perfect success. Readings of angles were taken at temperatures above the melting-points of the solids and the density of the solids was taken at the same temperatures. The solvent selected was a petroleum distillate with high boiling-point, 202° to 203°, 50 mm. that had been fractioned many times. It was essentially pure $C_{19}H_{38}$. On account of its high boiling-point there was no danger of loss by vaporization during the observations. The index and specific gravity of the solvent were determined at 60°, 70°, and 80°. The specific gravity was in all cases referred to water at 4°.

The following values were given by the solvent oil :

	Specific gravity.	Angle of refraction.	Index of refraction.
60°	0.7785	49° 6′	1.4341
70°	0.7722	49° 35′	1.4311
80°	0.7612	50° 16′	1.4277

The results of the observations were calculated by the formula for mixtures:

[1] Proc. Am. Acad., **32**, 365 (1902) ; This JOURNAL, **28**, 165 (1902).

$$\frac{n-1}{d}\ 100 = \frac{n_1-1}{d_1} + \frac{n_2-1}{d_2}\ (100-p).$$

n = index of mixture
n_1 =   "   " solvent
n_2 =   "   " solid
d = density of mixture $\Big)$
d_1 =   "   " solvent $\Big\}$ all taken at t°
d_2 =   "   " solid $\Big)$
p = per cent of solvent
$(100-p)$ =   "   " solid

The mixtures were made of such proportions that each contained approximately 20 per cent of the solid, and 2 grams were necessary for each determination, one-half the full capacity of the cup, which was necessary to maintain a uniform temperature. The index and specific gravity of each solid were taken at two temperatures, 60° and 70°, or 70° and 80°.

The following results were obtained with the hydrocarbons from Pennsylvania petroleum :

Distillate, 50 mm. 260° to 262°. $C_{23}H_{48}$.
Per cent of solvent, 77.86.
Per cent of solid, 22.14.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
60°	0.7780	0.7769	49° 9′ 3″	1.4337
70°	0.7711	0.7709	49° 43′	1.4304

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
60°	1.4432	110.61	
70°	1.4260	107.68	107.68

Distillate, 50 mm. 272° to 274°. $C_{24}H_{50}$.
Per cent of solvent, 82.53.
Per cent of solid, 17.47.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
60°	0.7785	0.7771	49° 5′ 3″	1.4341
70°	0.7734	0.7719	49° 40′	1.4307

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
60°	1.4432	113.08	
70°	1.4251	112.00	112.57

Distillate, 50 mm. 282° to 284°. $C_{25}H_{52}$.
Per cent of solvent, 84.03.
Per cent of solid, 15.97.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7724	0.7765	49° 50′	1.4297
80°	0.7618	0.7632	50° 23′ 8″	1.4263

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
70°	1.4241	115.0	
80°	1.4212	117.0	117.2

Distillate, 50 mm. 292° to 294°. $C_{26}H_{54}$.
Per cent of solvent, 83.13.
Per cent of solid, 16.87.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7726	0.7780	49° 38′	1.4309
80°	0.7618	0.7685	50° 13′ 7″	1.4373

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
70°	1.4320	122.0	
80°	1.4305	123.2	121.8

Distillate, 50 mm. 300° to 301°. $C_{27}H_{56}$.
Per cent of solvent, 77.64.
Per cent of solid, 20.36.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7719	0.7757	49° 55′	1.4292
80°	0.7623	0.7655	50° 29′ 4″	1.4257

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
70°	1.4206	124.2	
80°	1.4194	125.45	126.4

Distillate, 50 mm. 312° to 314°. $C_{28}H_{58}$.
Per cent of solvent, 86.79.
Per cent of solid, 13.21.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
$70°$	0.7738	0.7770	$49° 40' 6''$	1.4297
$80°$	0.7618	0.7669	$50° 14' 6''$	1.4272

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
$70°$	1.4184	126.6	
$80°$	1.4170	128.8	131

Having at hand a series of solid hydrocarbons separated from commercial paraffin, that correspond in composition to the solid hydrocarbons from crude Pennsylvania petroleum, determinations of the indices of refraction of these bodies were made for the purpose of comparison. The formulas of the paraffin hydrocarbons are given as they have been determined, although the results have not been published.

Distillate, 50 mm. 260° to 262°. $C_{23}H_{48}$.
Per cent of solvent, 79.84.
Per cent of solid, 20.16.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
$60°$	0.7780	0.7706	$49° 16' 5''$	1.4330
$70°$	0.7668	0.7641	$49° 44'$	1.4303

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
$60°$	1.4256	106.7	
$70°$	1.4374	111.0	108.0

Distillate, 50 mm. 282° to 286°. $C_{25}H_{52}$.
Per cent of solvent, 78.35.
Per cent of solid, 21.65.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
$60°$	0.7784	0.7779	$49° 10'$	1.4337
$70°$	0.7721	0.7707	$49° 46'$	1.4301

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
$60°$	1.4206	117.6	
$70°$	1.4194	117.0	117.2

Distillate, 50 mm. 300° to 302°. $C_{27}H_{56}$

Per cent of solvent, 82.81.

Per cent of solid, 17.19.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7727	0.7770	49° 50′	1.4297
80°	0.7625	0.7669	50° 13′	1.4272

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
70°	1.4287	123.4	
80°	1.4276	126.1	126.4

Distillate, 50 mm. 312° to 314°. $C_{28}H_{58}$.

Per cent of solvent, 79.75.

Per cent of solid, 20.25.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7737	0.7806	49° 42′	1.4305
80°	0.7630	0.7699	50° 15′	1.4277

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
70°	1.4285	129.3	
80°	1.4226	129.9	131

Commercial paraffin gave the following indices :

Per cent of solvent, 78.97.

Per cent of solid, 21.03.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
60°	0.7784	0.7788	49° 6′ 3″	1.4340
70°	0.7727	0.7732	49° 35′ 6″	1.4311

The results described above show a close agreement in the hydrocarbons separated directly from petroleum, and the corresponding bodies from paraffin, as well as the application of this method for obtaining the molecular refraction of solid bodies.

REPORT.

Moissan's Work on Silicides.

Among the binary compounds made by Moissan and his pupils are the silicides. As some interesting work on this class of compounds has appeared in the *Comptes rendus* during 1902, a report may be welcome. To this report is added a brief notice of the work on silicides by Moissan and his coworkers previous to 1902.

A New Hydride of Silicon.—The hydrides of silicon hitherto described are the gaseous SiH_4, made by Wöhler in 1857[1] by the action of dilute hydrochloric acid on impure magnesium silicide, and the solid yellow $(Si_2H_3)_n$ made by Ogier.[2] It should be noted that pure SiH_4 was first made by Friedel and Ladenburg by the action of sodium on tribasic silicoformic ether.[3]

Moissan and Smiles[4] tried to make pure SiH_4 by preparing the impure gas by Wöhler's method and fractioning it by the process devised by Moissan and Lebeau for separating the fluorides of sulphur.[5] Commercial magnesium powder was treated with ether to remove grease, with a powerful electromagnet to remove particles of iron, dried in a current of hydrogen, and mixed with powdered crystalline silicon made by the method of Vigouroux.[6] By heating this mixture in a current of pure, dry hydrogen a bluish, brittle mass is formed, from which the authors separated the crystalline portion and analyzed it, obtaining percentages close to those required for the compound $SiMg_2$. They consider it, however, to be rather a mixture of metal with one or more silicides. On treating it with dilute hydrochloric acid, a spontaneously inflammable gas escapes, which they prove to be hydrogen mixed with 4 to 5 per cent of SiH_4. Although the gas contained so little silicon hydride, they succeeded in fractioning it. The method depends on the assumption that in a gaseous mixture the constituents will have different freezing-points. In an apparatus filled with hydrogen, the magnesium silicide is decomposed by acid, the resulting mixture of gases washed, dried, and conducted slowly through a U-tube cooled to —180°. At this temperature the hydrides of silicon condense to a solid white mass, while the hydrogen in the mixture escapes. On

[1] Buff and Wöhler: Ann. chim. phys., [3], **52**, 257 (1858).
[2] Ogier: *Ibid.*, [5], **20**, 5 (1880).
[3] Friedel and Ladenburg: *Ibid.*, [4], **22**, 430 (1871).
[4] Moissan and Smiles: Compt. rend., **134**, 569.
[5] Moissan and Lebeau: *Ibid.*, **130**, 865.
[6] Vigouroux: Ann. chim. phys., [7], **12**, 153.

allowing the temperature in the U-tube to rise, the solid hy-drides melt, forming a colorless liquid which boils as the temperature rises, giving off pure gaseous SiH_4. A liquid hy-dride, stable at ordinary temperatures, remains in the tube. The authors repeated this experiment frequently, using magnesium silicide made in several operations, and always obtained the same results.

The liquid hydride boils at $52°$ and becomes solid at $-138°$. It takes fire spontaneously in contact with air or with chlorine. It reduces solutions of silver nitrate and mercuric chloride. When a little hydride is vaporized in a vessel filled with hydrogen the latter becomes spontaneously inflammable. Friedel and Ladenburg showed that pure SiH_4 is not spontaneously inflammable. Hence the liquid hydride acts toward SiH_4 as does the liquid phosphine toward the gaseous PH_3, which by contact with air becomes spontaneously inflammable. It is decomposed by solutions of alkalies, forming alkali silicate and hydrogen.

The analysis of the hydride,—decomposition by alkali, or by heat, and measuring the resulting hydrogen,—gave figures suggesting the composition Si_2H_6.

$$Si_2H_6 + 4NaOH + 2H_2O = 2Na_2SiO_3 + 7H_2.$$
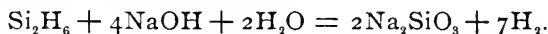
In a later article[1] the authors publish the results of a vapor-density determination of the hydride, confirming the composition Si_2H_6. They also give a detailed description of its properties. It can be heated to $100°$ without decomposition. It is a very energetic reducing agent. It acts curiously on certain saturated chlorides and fluorides. When brought in contact with carbon tetrachloride there is a violent explosion, forming amorphous carbon, amorphous silicon, and hydrochloric acid. Hexafluoride of sulphur is a new substance made by Moissan and Lebeau.[2] It is a gas so stable that sodium can be fused in a vessel filled with it without decomposing the gas. On mixing this gaseous SF_6 with the liquid Si_2H_6 there is a violent explosion, silicon, sulphur, and hydrofluoric acid being formed.

$$SF_6 + Si_2H_6 = S + 2Si + 6HF.$$
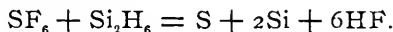
Lithium Silicide, Si_2Li_6.—Moissan[3] publishes the results of his attempts to make silicides derived from the hydride Si_2H_6. With potassium or sodium, derivatives he was not quite successful, although when he heated either of these metals in a vacuum with silicon, at the boiling-point of the metal very

[1] Moissan and Smiles : Compt. rend., **134**, 1549.
[2] Ann. chim. phys., [7], **26**, 145.
[3] Moissan : Compt. rend., **134**, 1083.

small quantities of silicide were formed. Better success awaited him with lithium. By heating a mixture of silicon with an excess of lithium in a vacuum at a dull red heat, he obtained a mixture of lithium silicide and lithium, from which he removed the lithium by distillation in a vacuum. The lithium silicide was in tiny indigo-blue crystals. Analysis shows it to have the composition Si_2Li_6. It dissociates, when heated in a vacuum, above 600°. Below this temperature hydrogen does not act on it; above 600° hydride of lithium is formed. If the silicide is warmed with fluorine it becomes incandescent, forming lithium fluoride and silicon tetrafluoride. The silicide behaves in much the same way toward chlorine, bromine, iodine, sulphur, and selenium. It is an energetic reducing agent. It exhibits a curious phenomenon when dropped into concentrated sulphuric acid; it becomes incandescent, fuses, and rolls about on the surface of the acid, as does potassium on the surface of water. The sulphuric acid is reduced to hydrogen sulphide and sulphur. When brought in contact with dilute acid or water it is violently attacked, forming a mixture of spontaneously inflammable hydride of silicon and hydrogen. But if means are taken to render the action of water very slow only hydrogen escapes. The explanation is that in the violent action Si_2H_6 is formed but decomposes mostly into SiH_4, H_2, and alkali silicate, while if the action is slow the reaction is

$$Si_2Li_6 + 6H_2O = Si_2H_6 + 6LiOH.$$
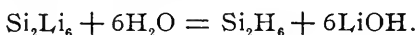
But as alkali decomposes the hydride, we get

$$4LiOH + Si_2H_6 + 2H_2O = 2Li_2SiO_3 + 7H_2.$$
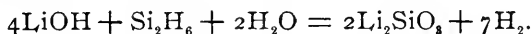
Cerium Silicides.—Ulik,[1] in 1865, while electrolyzing cerium fluoride, obtained a substance to which he assigned the composition Ce_2Si. Sterba,[2] working with Moissan, has studied the action of silicon on cerium oxide in varied proportions in the electric furnace. A definite crystalline substance of the composition $CeSi_2$ was the invariable result. This silicide crystallizes in opaque, steel-colored, brittle, microscopic crystals, is insoluble in water, does not react with hydrogen, reacts with oxygen or air only at high temperatures, reacts with cold fluorine with incandescence, and when warmed with chlorine, bromine, iodine, sulphur, or selenium, reacts with incandescence. It is attacked by hydrochloric and hydrofluoric acids.

[1] Ulik : Chem. Centrb., 1865, p. 1045.
[2] Sterba : Compt. rend., **135**, 170.

Cobalt Silicides.—Vigouroux,[1] in 1897, described a silicide of the composition $SiCo_2$, obtained by melting 10 parts of cobalt with 1 part of silicon. Its preparation and its properties recall those of the ferrous silicide, $SiFe_2$, studied by Moissan in 1895.[2] Lebeau,[3] in 1901, prepared a silicide, SiCo, by the action of copper silicide on cobalt at high temperatures, which resembled in its properties the iron silicide, SiFe. SiCo, like SiFe, can be dissociated, forming free silicon and $SiCo_2$. These analogies led Lebeau[4] to try to make a silicide, Si_2Co, to correspond with the third silicide of iron, Si_2Fe. He succeeded in preparing Si_2Co by heating cobalt with an excess of silicon, but he obtained it better crystallized by the action of copper silicide on a mixture of cobalt and silicon in the electric furnace. Si_2Co is obtained in small, dark-blue, octahedral crystals, which seem to belong to the regular system. It is a very stable substance, not attacked by oxygen, by nitric, sulphuric, or hydrochloric acids, or by alkalies. Hydrofluoric acid dissolves it, and fluorine changes it to CoF_2 and silicon tetrafluoride.

Previous Work on Silicides by Moissan and Co-workers.

Moissan : Compt. rend., **117,** 425. Silicide of carbon, CSi.
      " *Ibid.,* **119,** 1172. Fused iron carbide treated with silicon gives iron silicide and graphite.

Lévy : *Ibid.,* **121,** 1148. Titanium silicide, $SiTi_2$, by the action of titanium chloride on silicon at high temperatures.

Vigouroux : *Ibid.,* **121,** 711. Manganese silicide, $SiMn_2$, by the union of the elements in the electric furnace.

Vigouroux : *Ibid.,* **121,** 686. Nickel silicide, $SiNi_2$, and cobalt silicide, $SiCo_2$, by the union of the elements in the electric furnace.

Moissan : *Ibid.,* **121,** 621. Iron silicide, $SiFe_2$, chromium silicide, $SiCr_2$, by the union of the elements in the electric furnace.

Vigouroux : *Ibid.,* **122,** 318. Copper silicide, $SiCu_2$, by the union of the elements in the electric furnace.

Vigouroux : *Ibid.,* **123,** 116. Platinum silicide, $SiPt_2$. He finds that silicon does not combine directly with aluminium, lead, tin, antimony, bismuth, gold, or silver. He tried temperatures up to the volatilization of each metal.

Zettel : *Ibid.,* **126,** 833. Chromium silicide, $SiCr_3$, gray crystalline powder.

[1] Vigouroux : Ann. chim. phys., [7], **12,** 153 ; Compt. rend., **121,** 686.
[2] Moissan : Compt. rend., **121,** 621.
[3] Lebeau : *Ibid.,* **132,** 556.
[4] Lebeau : *Ibid.,* **135,** 475.

Lebeau : *Ibid.*, **128**, 1642.   Iron silicide, SiFe, by the action of copper silicide on iron.   This silicide was first made by Fremy by the action of silicon tetrachloride on iron.

Vigouroux : *Ibid.*, **129**, 1238.   Molybdenum silicide, Si_3Mo_2, by the action of silicon on molybdenum oxide in the electric furnace.

Lebeau : *Ibid.*, **131**, 583.   Silicon present as $SiFe_2$ in commercial ferrosilicon.

Moissan and Stock : *Ibid.*, **131**, 139.   Silicon borides, SiB_3, SiB_6, from boron and silicon in the electric furnace.

Lebeau : *Ibid.*, **133**, 1008.   Silicon is present in pig-iron as $SiFe_2$.

<div align="right">E. R.</div>

REVIEWS.

LEHRBUCH DER ANORGANISCHEN CHEMIE.   By PROFESSOR DR. HUGO ERDMAN.   3rd edition.   Braunschweig : Vieweg und Sohn.   1902.

The speedy appearance of 3,000 more copies of this work furnishes renewed evidence that in the popular mind its virtues exceed its defects.   The new edition is essentially similar to the preceding, and the reader is referred to the reviews already published concerning them.[1]   The new page (18) concerning force and work is very welcome, but it might have been amplified with advantage in a chemical direction.   The few words concerning the Phase Rule and the Law of Guldberg and Waage (pp. 135 and 731) do little to relieve the inadequacy of the theoretical treatment.   To those familiar with the somewhat wearisome discussion concerning the standard of atomic weights, it will be no surprise to learn that Erdmann continues to reject the excellent list prepared by his eminent compatriots ; but many will be surprised to see the atomic weights of all elements given with two decimal places.   This proceeding, of course, implies that the value for tantalum, for example, is known over ten times as accurately as that for oxygen, the numbers given being respectively 181.45 and 15.88.

On the other hand, it is probable that no other book of the same size records so great a variety of interesting experimental facts concerning inorganic substances.   T. W. R.

CELLULAR TOXINES, OR THE CHEMICAL FACTORS IN THE CAUSATION OF DISEASE.   By VICTOR C. VAUGHAN, M.D., LL.D., Professor of Hygiene and Physiological Chemistry and director of the Hygienic Laboratory in the University of Michigan, and FREDERICK G. NOVY, M.D., Sc.D., Junior Professor of Hygiene and Physiological Chemistry in the University of Michigan.   Fourth edition.   Philadelphia and New York : Lea Brothers & Co.   1902.   495 pp.

The fact that this is the fourth edition of this work since

[1] This JOURNAL, **20**, 847 (1898) ; **25**, 250 (1901).

1888 shows that the book has received the appreciation it deserves. It also gives a slight indication of the great progress that is being made in this line of work. Of necessity many changes have been made in this edition and much valuable matter added. The subject-matter has been brought up to 1902. The subjects now attracting the greatest amount of attention, namely, the theory of immunity, the specific precipitins and agglutinins, and the various cytolysins are lucidly discussed.

In connection with the theory of cytolysis, Ehrlich's graphic representations of the union of receptor, intermediary body, and complement are reproduced. The chemist is certain to be amused by these diagrams representing the union of supposedly definite chemical substances.

It must be remembered, however, that the diagrams were introduced merely to bring out clearly the relationship which is believed to exist between these bodies. The large amount of work which Ehrlich's theory has called forth has supported the theory and amply justified its promulgation.

The last two-thirds of the book is devoted to food poisoning and the chemistry of the ptomains and leucomains, to the literature of which the authors have contributed much. Most of the excellent bibliography of the previous edition has been omitted on account of lack of space. This is, of course, to be regretted. The references to the very recent work are given, however.

The book is of great value because of the importance of the subject-matter, which is well handled throughout. The original communications in this field are so scattered in the literature, and the nomenclature is so involved, that it is well-nigh impossible for those who are not working along these lines to keep up with the literature without the aid of such a book. It is the only book on the subject that is at all comprehensive, and should be within reach of all who are interested or working in this field of investigation.   A. S. L.

HIGHER MATHEMATICS FOR STUDENTS OF CHEMISTRY AND PHYSICS, WITH SPECIAL REFERENCE TO PRACTICAL WORK. By J. W. MELLOR, D.Sc., late Senior Scholar and 1851 Exhibition Scholar, New Zealand University; Research Fellow, The Owens College, Manchester. London, New York, and Bombay : Longmans, Green & Co. 1902.

The appearance of the admirable work in hand is most timely. If chemical students have a need which surpasses all others it is the need for at least an elementary knowledge of the higher mathematics. The day is past when this can be omitted from the training of a chemist.

While this is true, it must, however, not be forgotten that

there is a limit to the capacity and time of even the best students. The requirements to-day, of a student of chemistry, are not few in number. In addition to being a fair linguist he must have a close acquaintance with general physics, and if we expect him, in addition, to follow a long and elaborate course in differential and integral calculus and differential equations, we usually find that our expectations are disappointed. The object of the author can be seen best by quoting from his preface : '' It is almost impossible to follow the later developments of physical or general chemistry without a working knowledge of higher mathematics. I have found that the regular text-books of mathematics rather perplex than assist the chemical student who seeks a short road to this knowledge, for it is not easy to discover the relation which the pure abstractions of formal mathematics bear to the problems which every day confront the student of nature's laws, and realize the complementary character of mathematical and physical processes.

'' This work starts from the thesis that, so far as the investigator is concerned, higher mathematics is the art of reasoning about the numerical relations between natural phenomena ; and the several sections of higher mathematics are different modes of viewing these relations.''

The '' elementary'' part of the book treats of the differential calculus, coordinate or analytical geometry, functions with singular properties, the integral calculus, and infinite series and their uses.

The '' advanced'' portion deals with hyperbolic functions, how to solve differential equations, and Fourier's theories.

Under '' useful results'' we find chapters on how to solve numerical equations, determinants, probability and the theory of errors, a collection of formulas for reference, and reference tables.

The work is more than excellent, and is by far the best which has appeared in this field. It can not only be unconditionally recommended to all students of chemistry, but they are ardently urged to carefully study it if they wish to be able to follow the more recent developments in the theoretical side of their science. H. C. J.

AMERICAN

CHEMICAL JOURNAL

ON ACYLHALOGENAMINE DERIVATIVES AND THE BECKMANN REARRANGEMENT.

BY EDWIN E. SLOSSON.

A. W. Hofmann's[1] well-known method for preparing amines by converting acid amides into acid bromamides and treating the latter with aqueous alkali, involves a molecular rearrangement of the acid bromamides which, as Hoogewerff and van Dorp[2] later pointed out, is a perfect parallel of the Beckmann rearrangement of the oximes. In both cases an alkyl or alphyl radical (R) leaves the carbon atom holding the nitrogen halide (NHX), or the oxime (NOH) group, and attaches itself to the nitrogen atom, while the negative atom (Cl, Br), or group (OH), originally held by the nitrogen, oxidizes the carbon atom in question. The following equations give summarily the course of the reactions:

$$RCO.NHBr \longrightarrow BrCO.NHR \longrightarrow CO : NR + HBr ;$$
$$R'RC : NOH \longrightarrow R'C(OH) : NR \longrightarrow R'CO.NHR.$$
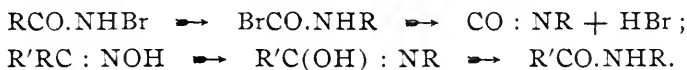
The mechanism of these interesting molecular rearrangements has been the subject of some investigation and quite a

[1] Ber. d. chem. Ges., **14**, 2725 (1881) ; **15**, 408 (1882).

[2] Rec. trav. chim. Pays-Bas, **6**, 376 (1887).

little speculation.[1] In a study of the nature and cause of the rearrangement, attention was called by Prof. Stieglitz to the desirability of determining experimentally to what extent, if at all, the hydrogen atom in the acid bromamide group, —CONHBr, is necessary for effecting the rearrangement of the acid bromamides. According to his views "an alkali might cause an acid bromamide, RCONHBr, to lose hydrobromic acid directly, thus producing a body, $(RCO)N\lt$, with a univalent nitrogen atom, the reactivity of which must then be the cause of the peculiar separation of the alkyl radical, R, from the carbon atom holding the nitrogen; the very reactive univalent nitrogen atom taking the alkyl radical away from the carbon atom, isocyanates must result, and these have actually been obtained as the first tangible products of the reaction." The formation of an isocyanate as the first product of the rearrangement is also in accord with the production of the most important compounds finally obtained from acid bromamides under varying conditions, *viz.*, amines by the action of hot dilute alkalies,[2] carbamates, RNHCOOK, in the presence of cold concentrated alkali,[3] and urethanes[4] in the presence of alcohols.

At the suggestion and under the direction of Professor Stieglitz, I undertook[5] the investigation of the problem whether the Beckmann rearrangement could still proceed or would be prevented when the hydrogen atom necessary for the breaking off of hydrobromic acid had been replaced by an alkyl or an alphyl group.

The investigation had to concern itself with the two possible classes of such derivatives. In the first place we could

[1] Hofmann : *Loc. cit.* ; Hoogewerff and van Dorp : Rec. trav. chim. Pays-Bas, **15**, 107 (1896). Freundler : Bull. Soc. Chim., **17**, 421 (1897) ; Nef : This JOURNAL, **18**, 753 (1896), Note. Ann. Chem. (Liebig), **298**, 305 (1897) ; **318**, 39, 227 (1901). See in particular, Stieglitz : On the " Beckmann Rearrangement," This JOURNAL, **18**, 751 (1896) ; **29**, 49 (1903).

[2] Hofmann : Ber. d. chem. Ges., **15**, 411, 412 (1882).

[3] Hoogewerff and van Dorp : *Ibid.*, **20**, Ref. 470 (1887).

[4] Stieglitz and Lengfeld : This JOURNAL, **15**, 215, 504 (1893).

[5] This work was begun in 1895 and has been continued, chiefly in summer vacations, ever since. A preliminary paper was published in 1896 (Ber. d. chem. Ges., **28**, 3266) to hold the field, and notices of the progress of the investigation have appeared at intervals (This JOURNAL, **18**, 753 (1896) ; Ber. d. chem. Ges., **34**, 1613 (1901) ; Proc. Chem. Soc. (London), **16**, 1 (1900), etc.)

have acylhalogenalkyl(alphyl)amines in which both the alkyl (alphyl) and the halogen are attached to the nitrogen atom, as in RCO.(NHalR'). In the second place we could have the halogen imido ethers RC(: NHal)OR', isomeric with the first series, the alkyl (alphyl) group, R', being attached to the oxygen atom. The work done on the former class of compounds will be discussed first.

When this investigation was begun only two or three compounds of this class were known. These were notably acetylethylchloramine prepared by Tscherniak and Norton,[1] and acetylchloranilide obtained by Bender.[2] Analogous bromine derivatives were not known. The methods used by the chemists mentioned failed to give good results in the preparation of other derivatives of this class, and of bromine compounds,[3] in particular, as most of these compounds are extremely sensitive to change by the action of acids, by reduction, by hydrolysis, or in the case of derivatives of the aromatic amines, by rearrangement into the acyl derivatives of halogen anilines, $H_2N(C_6H_4Hal)$. A careful study was first undertaken, therefore, to develop the special conditions and precautions for isolating these acyl halogen amides. As will be shown in the experimental part, this study was successful, both experimentally and in supplying the theoretical basis for correct work.

In the next place it was found necessary to make an experimental determination of the constitution of these acylhalogenalkyl(alphyl)amines, to decide between the two possible constitutions :

$$RCO.(NHalR') \quad \text{and} \quad RC(OHal)(: NR')$$
$$I. \qquad\qquad\qquad II.$$
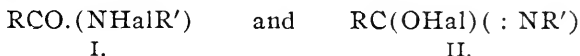
Although important theoretical conclusions were based[4] on the generally accepted constitution (I.), it really had never been proved rigidly, and it was open, if not to decided objec-

[1] Bull. Soc. Chim., **30**, 106 (1878).

[2] Ber. d. chem. Ges., **19**, 2272 (1886).

[3] See, for example, Castoro: Gazz. chim. ital., **28**, 312 (1898) ; Oechsner de Coninck : Compt. rend., **126**, 907, 1042 (1898).

[4] See, for example, Norton and Tscherniak : *Loc. cit.*, p. 106 ; Armstrong : J, Chem. Soc. (London), **77**, 1051 (1900) ; Chattaway and Orton : *Ibid.*, **75**, 1046 (1899) ; etc.

tion, at least to serious doubt. Its general acceptance seems to have been based chiefly on the idea that in an acyl anilide, such as acetanilide, $CH_3CONHC_6H_5$, the nitrogen atom still holds a hydrogen atom, as in aniline, and that such a compound must, by substitution, under the influence of hypochlorous acid, give a nitrogen halide, $CH_3CO.NClC_6H_5$. It has, however, been proved that acyl amides and anilides frequently do give oxygen derivatives.[1] For instance, Comstock and Kleeberg showed that formanilide forms a silver salt from which methylphenylimidoformate, $HC(OCH_3)NC_6H_5$, is obtained by the action of methyl iodide. The metal salts undoubtedly have an analogous constitution.[2] On finding that silver formanilide gave with iodine, under the same circumstances as in the previous reaction, formyliodaniline, Comstock suggested that the iodine derivative could very well have a constitution analogous to that of the imido ethers, *viz.*, $HC-(OI) : NC_6H_5$, and since the iodide has the same properties as all the acylchlor- and bromanilides, it is obvious that the constitution of the latter bodies could not be based on their formation from acyl anilides. Their properties of being chlorinating or brominating agents, of being susceptible to hydrolysis, and of being readily rearranged into acyl derivatives of chlorinated or brominated anilines, $NH_2(C_6H_4X)$, would agree equally well with either of the above constitutions (I. and II.). If the bodies were not really nitrogen halides, $RCON(Hal)R'$, however, any deductions in regard to the "Beckmann rearrangement," as based on their behavior, would obviously have been impossible, and so a rigid experimental proof was sought at once, which would decide between constitutions I. and II.

In our first attempts to settle the question of the constitution of these bodies their behavior was such as to throw considerable doubt on their being nitrogen halides. We found first that the acyl halogen anilides do not form any cyanogen derivatives with potassium cyanide according to the equation :

[1] Comstock, Kleeberg, Wheeler, and others : This JOURNAL, **12**, 493 (1890) ; **13**, 520 (1891) ; **19**, 129 (1899) ; etc. Tafel and Enoch : Ber. d. chem. Ges., **23**, 105 (1890) Stieglitz and Dains : J. Am. Chem. Soc., **21**, 135 (1899).

[2] Hantzsch : Ber. d. chem. Ges., **34**, 3142 (1901) ; **35**, 228 (1902).

$$CH_3.CO.N(Hal).C_6H_5 + KCN \longrightarrow$$
$$CH_3.CO.N(CN).C_6H_5 + KHal,$$
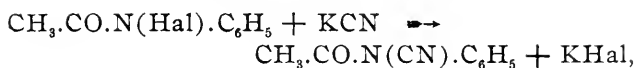
but are always reduced to the acyl anilides. On the other hand, undoubted nitrogen chloride derivatives, like the chlordialkylamines, R_2NCl, easily give cyanamides under exactly the same conditions.[1]

$$R_2NCl + KCN \longrightarrow R_2N.CN + KCl.$$

In order to make sure that the right conditions were present for Berg's reaction, the method was tried on chlorpiperidine, and cyanpiperidine was obtained without difficulty.

Secondly, it appeared from many experiments that the acylhalogenalkyl(alphyl)amines, by treatment with zinc ethyl, are simply reduced and not alkylated; for instance, the reaction

$$2R—CO—N(Hal)—C_6H_5 + Zn(C_2H_5)_2 \longrightarrow$$
$$2RCO—N(C_2H_5)(C_6H_5) + ZnHal_2$$
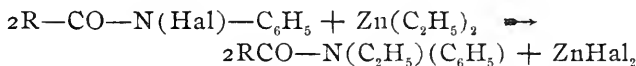
does not take place. But an undoubted nitrogen chloride derivative, ethyldichloramine, $C_2H_5—NCl_2$, is known to give, with zinc ethyl, triethylamine.[2]

The last way taken for establishing the constitution of the acylhalogenalkylamines led to the following simple solution of the question.[3] If acetylamylamine is treated with hypochlorous acid, the corresponding acetylchloramylamine is formed:

$$CH_3CO—NH—C_5H_{11} + HOCl \longrightarrow$$
$$CH_3CO—NCl—C_5H_{11} + H_2O.$$
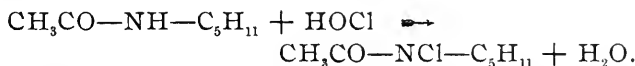
The same compound is obtained when amylchloramine[4] is acetylated by means of acetic anhydride,

$$C_5H_{11}—NHCl + (CH_3CO)_2O \longrightarrow$$
$$CH_3CO—NCl—C_5H_{11} + C_2H_4O_2.$$
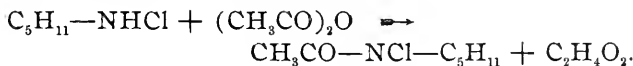
This result proves that the acylhalogenalkylamines and anilides are really nitrogen halides, that is, derivatives of Hofmann's acid chlor- and bromamides, $RCO(NHHal)$, and that

[1] Berg : Ber. d. chem. Ges., **26**, 188 (1893), Ref.

[2] Tscherniak : *Ibid.*, **9**, 148 (1895).

[3] Stieglitz and Slosson : *Ibid.*, **34**, 1615 (1901).

[4] Berg : Bull. soc. chim., [3], **3**, 687 (1890).

the constitution, $RC(OHal)(NR')$, suggested by Comstock as a possible one for them, may now be excluded without hesitation as far as the chlorine and bromine compounds are concerned.[1]

Two parts of the work on the first class of alkyl (alphyl) derivatives of the acid halogen amides, *viz.*, the determination of the special conditions for preparing them and the determination of their constitution, having been disposed of, it only remained to test whether such compounds could be made to suffer the '' Beckmann rearrangement'' which the mother-substances, the acid halogen amides, $RCO—NH—Hal$, undergo so readily. A large number of experiments with all varieties of acylhalogenalkylamines and acylhalogenalphyl-amines led to the important conclusion that in no case could a Beckmann rearrangement be effected. In some cases, for example, with benzchloranilide, $C_6H_5.NCl.C_6H_5.CO$, it was possible to show that the rearrangement did not occur even to a minimal extent, since not even traces of diphenylamine, which is easily detected, could be found.

It was shown above, (page 291) that the acid halogen amides must give by replacement of the hydrogen atom of the group $—CONHHal$, besides the alkylated (alphylated) nitrogen derivatives $—CO(NRHal)$ just discussed, a second class of isomeric ethers, $—C(OR)(: NHal)$, whose relation to the Beckmann rearrangement was included in this investigation. In contrast to the bodies just dealt with, these imido ethers presented a comparatively simple problem. The methods for their preparation and their constitution had been definitely established by Stieglitz,[2] who prepared methyl chlor- and bromimidobenzoate, and they had been proved by him to be most remarkable for their stability as nitrogen halides. My work on these bodies was chiefly directed towards the preparation of stereoisomers and the effecting of the Beckmann rearrangement. On the basis of Hantzsch and Werner's[3] theory

[1] So little is known about the corresponding iodine derivatives, and the character of hypoiodous acid approaches so near that of a base that no conclusion as to the constitution of Comstock's formiodanilide should be based on the above work with hypochlorous acid. Formiodanilide may very well stand closer to silver formanilide than to formchloranilide.   J. STIEGLITZ.

[2] This JOURNAL, **18**, 751 (1896).

[3] Ber. d. chem. Ges., **25**, 33 (1892) ; **29**, 1146 (1896).

of stereoisomerism (syn and anti) produced by a doubly-linked nitrogen atom, as in the oximes, the halogen imido ethers might exist in the two stereoisomeric forms,

$$\begin{array}{ccc} R—C—OR' & & R—C—OR' \\ \parallel & \text{and} & \parallel \\ Hal—N & & N—Hal \end{array}.$$
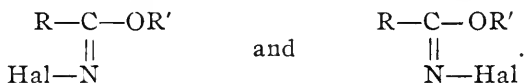
Only the former class would be expected to be directly capable of undergoing a Beckmann rearrangement of the molecule.[1] Although solid chlorimido ethers of admirable stability were obtained, all efforts at recognizing stereoisomers, or at converting the compounds obtained into other modifications, resulted in failure.[2] None of the halogenimido ethers investigated gave the least sign of undergoing the Beckmann rearrangement.

It would appear, therefore, that the presence of the hydrogen atom (H') of the acylamine halides, RCO—NH'Hal, is essential for the successful " Beckmann rearrangement" of the molecules, since neither class of their alkyl derivatives is capable of undergoing the rearrangement in question.

<center>EXPERIMENTAL PART.</center>

The Preparation of Alphylacylhalogenamines.

The successful preparation of the chlorine and bromine compounds of this class was found to be dependent on observing a number of interesting conditions, which follow from the peculiar tendency of these bodies to suffer chemical change. Bender had obtained phenylacetylchloramine by treating acetanilide with an aqueous extract of bleaching-powder and acidulating the mixture with acetic acid. His directions are so indefinite that some chemists have failed entirely to prepare phenylacetylchloramine by his process. For example, Castoro[3] says Bender's reaction is impossible

---

[1] Werner : *Loc. cit.*

[2] Like failure, it will be remembered, has so far attended all efforts of Hantzsch and others to prepare stereoisomeric derivatives, : C : NX, in which X was, for instance, C_6H_5—, —COOR, or any group in fact other than —OH (the oximes) or —NHAlphyl (the hydrazines). Ber. d. chem. Ges., **27**, 1248 (1899), etc.

[3] Gazz. chim. ital., **28**, 312 (1898) ; compare Armstrong : J. Chem. Soc. (London), **77**, 1047 (1900).

and that he gets by all possible variations of the proportions of acetanilide, acetic acid, and hypochlorite no active nitrogen halide derivatives but only two inactive bodies, parachloracetanilide and a dichloracetanilide.[1] While, as a matter of fact, the active acetylchloranilide can readily be obtained by following Bender's directions carefully, neither the yield nor the purity of the compound is satisfactory. The method failed utterly in attempts to use it for preparing analogous active nitrogen bromide compounds of the acylanilides,[2] only inactive derivatives of the bromanilines resulting with the bromine attached to the benzene nucleus of the anilines.

The first fact of which cognizance must be taken in the preparation of these nitrogen halides is that the reaction by which they are formed is reversible :[3]

$$RCO—NHR' + HOHal \; \rightleftarrows \; RCO—NHalR' + H_2O.$$
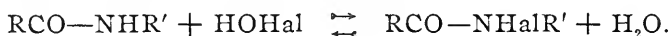
The mass law requires, therefore, an excess of hypochlorous or hypobromous acid to effect a tolerably complete transformation except in those cases where the product is very insoluble. In going from the derivatives of hypochlorous to hypobromous and hypoiodous acid, the hydrolysis of the above nitrogen halides by water seems to become progressively more marked, and, therefore, to play a more important rôle in their preparation, as the atomic weight of the halogen increases. This was verified experimentally. The phenylacylbromamines were found by me to stand between the analogous chlorine and iodine derivatives. Phenylacetylchloramine is rather stable even towards boiling water, phenylacetylbromamine can be prepared in the presence of water, but it is slowly decomposed, even at ordinary temperatures, by water (see below), and phenylformyliodamine could be prepared[4] only when water was carefully excluded.

In the next place, where R' in the above reaction is an aromatic radical, the nitrogen halide with its reactive halogen

[1] Oechsner de Coninck (Compt. rend., **126**, 907, 1042 (1898)) obtained **no** nitrogen halides by the action of hypochlorites on amides and amines.

[2] Slosson : Ber. d. chem. Ges., **28**, 3266 (1896) ; see also Seliwanow : *Ibid.*, **25**, 3620 (1892) ; Jacoby : J. prakt. Chem., [2], **37**, 50 (1888).

[3] Seliwanow : *Loc. cit.*

[4] Comstock and Kleeberg : This JOURNAL, **12**, 500 (1890).

atom is very readily transformed into the stable isomeric acyl derivative of the halogenated anilines, according to

$$RCO.NHalC_6H_5 \; \rightleftharpoons \; RCO.NH(C_6H_4Hal).$$

As the latter reaction is non-reversible, the preparation of the nitrogen halides may prove an utter failure if this transformation is not prevented. This is the chief source of failure in making these compounds. The transformation was found to proceed gradually under the influence of moisture, and very much more rapidly by the action of acids. It is also caused by the action of heat.[1]

As the phenylacylbromamines are much more sensitive to water and acids (see below) than the chloramines, only their transformation-products are obtained if acids even of ordinary weakness (*e. g.*, acetic acid) are used in preparing them. The hypobromous acid necessary for their formation must be liberated by such weak acids as boric acid[2] or carbonic acid,[3] the concentration of whose hydrogen ions can be still further

---

[1] The first two influences are undoubtedly identical fundamentally, water being an exceedingly weak acid. The slow transformation under the influence of water, the vastly increased rate of change in the presence of acids, and the fact that a number of these compounds when dry (see pages 304–5 below) are comparatively stable towards heat and are only very slowly transformed by it, indicate that in aqueous solution this transformation is due rather to a sequence of two reactions, *viz.* :

$$RCO.NHalC_6H_5 + H_2O \; \rightleftharpoons \; RCO.NHC_6H_5 + HOHal \quad (1),$$

and $$RCO.NHC_6H_5 + HOHal \; \rightarrow \; RCO.NHC_6H_4Hal + H_2O \quad (2),$$
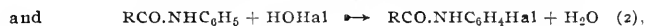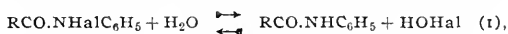
than to a direct molecular rearrangement or migration of atoms :

$$RCO.NHalC_6H_5 \; \rightarrow \; RCO.NHC_6H_4Hal \quad (3).$$
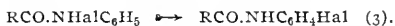
As the acylalphylbromamides are much more sensitive to water and acids than the chlorides, we find in this behavior the reason why they were never successfully isolated and the transformation-products alone were obtained, until in 1896 Slosson and I avoided the use of any but the weakest acids in preparing them. (See Stieglitz and Slosson : Ber. d. chem. Ges., **28**, 3267 (1896) ; Proc. Chem. Soc. (London) **16**, 1 (1900) ; Armstrong : J. Chem. Soc. (London), **77**, 1047 (1900) ; Chattaway and Orton : *Ibid.*, **77**, 134 (1900)). Whether the transformation under the influence of heat is due to a molecular rearrangement or, rather, to a mutual chlorination (bromination) of two molecules,

$$2RCO.NHalC_6H_5 \; \rightarrow \; 2RCO.NHC_6H_4Hal,$$
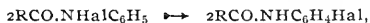
remains an open question, which could be decided by determining the velocity of the reaction. Since this was written Blanks has shown by velocity determinations that the reaction consists of a monomolecular rearrangement. Rec. trav. chim. Pays-Bas., **21**, 366 (1902). See also Armstrong : *Loc. cit.* J. Stieglitz.

[2] Slosson : *Loc. cit.*

[3] Slosson : *Loc. cit.* ; Chattaway and Orton : J. Chem. Soc. (London), **75**, 1046 (1899), etc. ; Küster : Ztschr. Elektrochem., **4**, 110.

diminished by using a bicarbonate, or carbonic acid in the presence of a bicarbonate.

In the last place it follows from the above discussion that in the purification of these nitrogen halides by recrystallization, aqueous solvents and moisture must be rigidly excluded, besides, obviously, such solvents as are very easily chlorinated or brominated.

The conditions, then, for successfully preparing even rather unstable representatives of the alphylacylhalogenamines are the use of a considerable excess of the hypo acid, the exclusion of more than minimal quantities of hydrogen ions, best obtained from very weak acids, and the exclusion of moisture in the process of purification. The avoidance of an unnecessary rise of temperature may be added as a further precaution.

For chlorinating compounds insoluble in water the following method was found useful : Thirty grams of sodium hydroxide are dissolved in 100 cc. of water and a weighed amount of chlorine, nearly enough to saturate it, is absorbed in the cold solution. With ordinary caustic soda, which has been exposed to the air and therefore has taken up some water and carbonic acid, between 20 and 24 grams of chlorine may safely be absorbed, but the operation must be stopped before decomposition sets in through an excess of chlorine. A solution so prepared contains very nearly the theoretical amount of active chlorine, one-half the total. It can be kept in a cool place for several days without material loss of strength. If to a sufficient quantity of this solution be added the calculated amount of the amide dissolved in alcohol, which is saturated with boric acid, the chlorine compound is precipitated on diluting with water, and can be filtered by suction and dried on a porous clay plate ; or, if it is very unstable, the reagents may be mixed in a separatory funnel, together with powdered ice, and the nitrogen halide extracted at once with ether. Bromine compounds can be made in the same way, by using a solution prepared by dissolving bromine in a slight excess of potassium hydroxide solution, or by shaking it with mercuric oxide and water.

All the nitrogen halides set free iodine, either from potas-

sium iodide or from hydriodic acid, and they can be analyzed
by dropping them into a slightly acidified solution of potas-
sium iodide and titrating the released iodine with a $N/10$ solu-
tion of thiosulphate.   Where the compound is very insoluble
in water, it is necessary to dissolve it in alcohol or in a mix-
ture of ether and alcohol.   The determination of the halogen
as silver halide does not necessarily indicate the purity of the
compound in the case of anilides and naphthalides, because
the isomers with halogen in the ring, which are the chief im-
purities, give by Carius' method the same analytical figures
as the nitrogen halides. It is best to titrate the iodine as quickly
as possible, for there are sometimes secondary reactions with
the free iodine which cause too low results.[1]

<p style="text-align:center;">*Phenylacetylchloramine* (*Acetylchloraminobenzene*),
$CH_3CO—NClC_6H_5$.</p>

This compound may be formed in acid, alkaline, or neutral
solutions of hypochlorites, but a slightly alkaline solution is
best, and, after trying a great many methods, the following
was found to give the most satisfactory results:[2] Twenty
grams of acetanilide are dissolved in 4 liters of water and the
solution cooled to at least 10°. Chlorine is passed into a
cold solution of sodium carbonate (10 per cent) until a test
with a few cubic centimeters shows that the solution will pre-
cipitate ten times its volume of the acetanilide solution ; then
the required quantity of this hypochlorite solution is poured
into the acetanilide solution and shaken.   The chlorine com-
pound comes down at once as a flocculent precipitate.   It is
filtered, washed, and dried.   The yield is 20 to 24 grams
(theoretical 25 grams).   If the hypochlorite solution is de-
ficient in strength or quantity, the precipitate forms slowly in
fine needles, isolated or in bundles.   If too strongly alkaline,
the solution turns brown, has the odor of isocyanide, and the
chlorine compound reverts to acetanilide.   If the solution is
too strongly acid, or if there is much free chlorine, para-
chloracetanilide is the sole product.   Phenylacetylchloramine

[1] Compare Behrend and Schreiber : Ann. Chem. (Liebig), **318**, 381 (1901).

[2] For other methods, see Bender : Ber. d. chem. Ges., **19**, 2272 (1886) ; Chattaway
and Orton : J. Chem. Soc (London), **79**, 277 (1901) ; Armstrong : *Ibid.*, **77**, 1047 (1900).

is quite stable when pure and dry, and it can be preserved for days without material decomposition. It melts at 91°.

0.2463 gram substance required 28.98 cc. N/10 thiosulphate.

	Calculated for C_8H_8NOCl.	Found.
Cl	20.91	20.86

A great many experiments were made on the decomposition of phenylacetylchloramine with potassium hydroxide and sodium methylate, but in no case was it possible to detect methylaniline or any derivative of it, which would be the product if a Beckmann rearrangement had taken place. From 18 to 30 grams of the substance were used in each test, but acetanilide was the sole product identifiable whether the reaction-product was worked out by precipitation, extraction, or distillation. Both hot and cold solutions of potassium hydroxide were used, and both 10 and 20 per cent strengths. When hot strong alkali was used, the solution turned brown and had a disagreeable odor, apparently of isocyanide, and there was a little tarry matter formed. The acetanilide was, however, recovered almost quantitatively in every case in a nearly pure state, and from the slight residues the only basic compound obtained after saponification was aniline in which no methylaniline could be detected.

A series of experiments with solutions of sodium methylate, cold and hot, strong and weak, gave similar results, and none of the products of a Beckmann rearrangement could be found. Even when 30 grams of the chlorine compound were used, acetanilide was the sole product in quantity sufficient to identify, although there was evidence of further decomposition in the red color of the extract in ligroin, which in acid alcohol gave a purple solution of great tinctorial power.

Methyl Phenylmethylcarbamate, $(C_6H_5NCH_3)COOCH_3$.—As this compound is one which might result from a Beckmann rearrangement of phenylacetylchloramine with sodium methylate, its properties were determined by preparing it. Redistilled methylaniline (16 grams) was shaken with the same volume of water to an emulsion, and to the solution cooled to 0° was added 7 grams of methyl chlorcarbonate from small

bulbs with capillary tubes. The mixture was warmed for half an hour, then cooled, and hydrochloric acid added to acid reaction. The ether extract was dried over calcium chloride and distilled twice. The product, the methyl ester of phenylmethylcarbamic acid, is a light-yellow oil, easily soluble in ether and ligroin. It is dissolved by heating it in concentrated hydrochloric acid but is not attacked by a solution of sodium hydroxide. It has a fishy odor and boils at 235°.

0.4070 gram substance gave 44 cc. N at 25° C. and 743.8 mm.

	Calculated for $C_9H_{11}O_2N$.	Found.
N	8.42	8.43

Several attempts were made to replace the chlorine atom in phenylacetylchloramine with an ethyl radical by the use of zinc ethyl,[1] but in no case was there evidence of such a reaction.

Dry phenylacetylchloramine (14 grams) was dropped gradually into a solution of zinc ethyl (5 grams) in absolute ether in a flask fitted with a reflux condenser. At each addition of the chloranilide there was an evolution of a gaseous hydrocarbon, which was collected but not analyzed. A stream of carbon dioxide was carried through the apparatus during the operation. At the end the ether was evaporated and water added. Repeated extraction of the acid and alkaline solution with ether gave acetanilide as the only product, and this, when purified, amounted to 11.3 grams. Repeating the experiment with the same quantities of the reagents, parachloracetanilide was the chief product obtained. Evidently the molecular transformation was caused by the energy liberated in the reaction. In the residues the products of saponification, acetic acid and aniline were found in small quantity, but no derivatives of ethylaniline which would result from the substitution of chlorine by that radical or methylaniline from a Beckmann rearrangement could be detected.

Phenylacetylchloramine (13 grams) dissolved in 50 per cent alcohol and treated with potassium cyanide (5 grams) gave acetanilide and parachloracetanilide as the sole products.

[1] Tscherniak : Bull. soc. chim., [2], **25,** 166 (1896) ; Ber. d. chem. Ges., **9,** 148(1896).

There was no evidence of the substitution of chlorine by cyano-
gen according to Berg's reaction.[1]

Piperidyl Cyanide by Berg's Reaction.—In order to test the
generality of Berg's reaction and to assure myself that I un-
derstood the conditions under which it took place, piperidyl
cyanide was prepared by the following method.[2]   Six grams
of chlorpiperidine, prepared by dropping 10 grams of piperi-
dine into a boiling solution of bleaching-powder,[3] was dis-
solved in alcohol and treated with 3 grams of potassium
cyanide in fine powder.   The reaction takes place imme-
diately and the alcohol is heated to boiling.   After distilling
off the alcohol, taking up the residue with ether, and drying
it over potassium hydroxide, the piperidyl cyanide was dis-
tilled in a vacuum (30 mm.) between 122° and 124° C.   It is
a colorless, fragrant oil, insoluble in water.

The identity of the piperidyl cyanide was proved by con-
verting it into piperidyl urea by heating it with 50 per cent
sulphuric acid for half an hour on a water-bath.   After neu-
tralizing the solution with sodium hydroxide and extracting
the mixture with ether, the urea was obtained by evaporation
of the ether.   It was recrystallized from water and compared
with piperidyl urea made by Cahours' method.[4]   A mixture
of the two preparations melted at the same point (103° C.).

Parachloraniline.—On account of the ease with which the
chlorine in acetylchloranilide can be made to enter the para
position and the resulting compound can be saponified, use can
be made of this reaction in the preparation of *p*-chloraniline.
For making this in quantity, the following process was found
more convenient than the methods published :   Dissolve 10 to 15
grams of acetanilide in a liter of water, cool somewhat, and
pass in chlorine as long as the white precipitate of *p*-chlor-
acetanilide is formed.   Filter and heat the chloracetanilide for
an hour at 150°, with enough concentrated sulphuric acid to

1 Ann. chim. phys., [7], **3,** 353 (1894).

2 The same cyanide has since been prepared in another way by Wallach and
Samann : Ber. d. chem. Ges., **32,** 1873 (1899).

3 Lellmann and Geller ; *Ibid.*, **21,** 1922 (1888).

4 Ann. chim. phys., [3], **38,** 84 (1853).

dissolve it. Pour the mixture into water, make the solution alkaline with some hydroxide to precipitate most of the parachloraniline, and extract the filtrate with ether to get the rest. Purify the compound by dissolving it in water, boiling the solution with animal charcoal, and filtering. By concentrating the water solution, parachloraniline crystallizes out in cubes or needles. The yield is almost quantitative.

Phenylacetylbromamine (Acetylbromaminobenzene),
$CH_3CO(C_6H_5NBr)$. —This compound was first made by adding a solution of potassium hypobromite to a saturated aqueous solution of acetanilide and then passing a stream of carbon dioxide into the solution. If the acetanilide solution contains borax or boric acid, the bromine compound is precipitated without using carbon dioxide. A saturated solution of acetanilide, prepared by dissolving about 5 grams in a liter of water and saturating it with borax and boric acid, is cooled to 0° and filtered. To this is added an excess, even twice the theoretical amount, of hypobromite solution made by dissolving bromine in 10 per cent potassium hydroxide. If both solutions are kept cold, best with powdered ice, the phenylacetylbromamine is slowly precipitated, and after filtering can be freed from a small quantity of parabromacetanilide by fractional crystallization from ether or ligroin. It is precipitated in yellow flakes or four-pointed stars, and melts at 94° to 95°, changing to parabromacetanilide.

0.1748 gram substance required 16.32 cc. N/10 thiosulphate.

	Calculated for C_8H_8ONBr.	Found.
Br	37.35	37.34

This bromacetanilide is very much more unstable than the corresponding chlorine compound, and changes into parabromacetanilide in a few minutes when in warm and moist air. With ammonium hydroxide it gives off nitrogen as do all the compounds of this class. In numerous experiments with this compound only the two forms of decomposition were observed : with acids, it is transformed to parabromacetanilide, and with alkalies acetanilide is regenerated. None of the products of a Beckmann rearrangement were ever found.

Phenylformylchloramine (*Formylchloraminobenzene*), HCO. $NClC_6H_5$.—This compound is precipitated in crystalline form by adding a solution of hypochlorous acid, made by running chlorine into a 10 per cent solution of sodium carbonate, to an ice-cold, saturated, aqueous solution of formanilide and shaking violently. The strength of the hypochlorous solution is ascertained by titration and an excess is used. The substance melts at 44°. It can be heated even to 120° without much decomposition. Above this temperature it gives off acid vapors accompanied with a slight odor, apparently of isocyanate. It can be recrystallized from ether, ligroin, or acetic acid, but it decomposes violently with ammonia, or when heated with absolute alcohol. Hydrochloric acid and many other reagents convert it into the isomeric formyl-*p*-chloranilide.

0.1273 gram substance required 16 cc. N/10 thiosulphate.

	Calculated for C_7H_6ONCl.	Found.
Cl	22.79	22.34

For comparison, formyl-*p*-chloranilide was also made by boiling 1 gram parachloraniline with 3 grams formic acid for half an hour. The excess of formic acid is distilled off and the residue poured into cold water. It melts at 101° C. It is soluble in ether, chloroform, or hot water, but insoluble in ligroin. Recrystallized from ether it forms colorless parallelograms with diamond markings, similar in form to methylbenzamide.

Phenylformylbromamine (*Formylbromaminobenzene*), $HCO—NBrC_6H_5$.—To prepare this a one per cent solution of formanilide in water, saturated with boric acid, is cooled to 0° and a little more than the calculated quantity of potassium hypobromite solution is added. Instead of using boric acid, a stream of carbon dioxide may be run in after the addition of the hypobromite. In either case a light-brown precipitate of formylbromaminobenzene is slowly formed, which can be recrystallized from ether or ligroin in needles which are only slightly yellow and melt at 79° to 80°. The compound decomposes spontaneously even in dry air, and attacks ammonia

water violently, giving off nitrogen. By acids, alkalies, and heat it is readily converted into parabromformanilide (m. p. 119°).

0.1678 gram substance required 16.6 cc. N/10 thiosulphate.

	Calculated for C_7H_6ONBr.	Found.
Br	39.95	39.55

Phenylbenzoylchloramine (Benzoylchloraminobenzene),
$(C_6H_5CO)NClC_6H_5$.—The insolubility of benzanilide in water makes it rather difficult to prepare the chlorine derivative by the customary methods,[1] but the following procedure gives a good yield of excellent purity. Two grams of benzanilide are dissolved in 200 cc. of alcohol with 10 grams of boric acid. To this is added 10 cc. of a solution of sodium hypochlorite containing 0.07 gram or more of active chlorine per cubic centimeter, both solutions being kept cold. After shaking and filtering the mixture with the pump, water is added and the benzoylchloraminobenzene appears as a white, flocculent precipitate. It is filtered and dissolved in ether. On adding light ligroin and evaporating the mixture in a vacuum-desiccator it forms large, transparent crystals.

0.1091 gram substance required 9.39 cc. N/10 thiosulphate.

	Calculated for $C_{13}H_{10}NOCl$.	Found.
Cl	15.30	15.22

The substance is easily soluble in ether and alcohol but less soluble in ligroin. It melts, without decomposition, at 81°.5 to 82°,[1] and it is still active with potassium iodide after it has been heated to 160° and turned slightly yellow. Above this temperature it becomes rapidly darker and gives off a little vapor, which is, judging from its odor, benzoyl chloride. The chief substance formed, however, is parachlorbenzanilide. This compound is also the result of boiling with water. Ammonium hydroxide attacks the nitrogen halide slowly in alcoholic solution.

Phenylbenzoylchloramine dissolved in alcohol and treated with a little sodium hydroxide and warmed, is reduced at

[1] Slosson: Ber. d. chem. Ges., **28**, 3269 (1896); Chattaway and Orton: J. Chem. Soc. (London), **75**, 1053 (1899). They give the melting-point as 77°.

once to benzanilide, as was proved by taking the melting-point of the reaction-product mixed with known benzanilide. The crude product of the reaction tested for diphenylamine by hydrochloric and nitric acids gave no coloration. A portion of the same mixture, to which a minute particle of diphenylamine had been added, gave an intense indigo-blue. So it is positive that the Beckmann rearrangement does not take place to the slightest extent.

For comparison with the product obtained from benzoyl-chloraminobenzene by the migration of the chlorine atom from the nitrogen to the aromatic nucleus, parachlorbenzanilide was prepared from benzoyl chloride and parachloraniline. When recrystallized from hot water, it appeared in fine cubical crystals. It had the melting-point 187° to 187°.5, instead of 183° to 184° as reported by Hantzsch.[1]

Paratolylformylchloramine (*Formylchloramino-p-toluene*), $CHO.NClC_6H_4CH_3$.—Adding 20 cc. of a 10 per cent solution of formyl toluide in alcohol with a little acetic acid to 100 cc. of a solution of bleaching-powder (1 cc. $=$ 0.008 gram chlorine) precipitates formylchlortoluide. When dissolved in hot ligroin, it separates, on cooling, in beautiful clusters of crystals, melting at 49° to 50° and decomposing at 140°.

0.1122 gram substance required 13.09 gram $N/10$ thiosulphate.

	Calculated for $C_8H_8NOCl.$	Found.
Cl	20.94	20.77

Paratolylformylbromamine (*Formylbromamino-p-toluene*), $CHO—NBrC_6H_4CH_3(p)$.—To prepare this a saturated solution of formyl paratoluide in water is added to an ice-cold solution of potassium hypobromite until a flocculent precipitate is formed. The bromine compound slowly forms in flakes by shaking. It is filtered rapidly, dissolved in a very little ether, several times its volume of light ligroin is added, and the solution is quickly evaporated by a blast or by a vacuum-pump. It is pure white and melts at 80°, decomposing at slightly higher temperatures. It is extremely unstable

[1] Ber. d. chem. Ges., **24**, 56 (1891).

and rapidly turns red on exposure to moist air, giving off free bromine.

0.1314 gram substance required 11.60 cc. N/10 thiosulphate.

	Calculated for C_8H_8ONBr.	Found.
Br	37.35	35.30

α-Naphthylformylchloramine (*Formylchloramino-α-naphthalene*), HCO—($C_{10}H_7NCl$).—Adding an alcoholic solution of formyl-α-naphthalide with a little acetic acid to a large amount of calcium hypochlorite solution gives, after a few minutes' shaking in the cold, a precipitate of the chloramine. It is very soluble in chloroform but crystallizes best from ligroin. The melting-point is 63°. It is extremely unstable, as it is decomposed quickly by water at ordinary temperatures. An ethereal solution, brought over caustic potash to dry it, is at once attacked, the ether boiling and turning red.

0.1146 gram substance required 9.8 cc. N/10 thiosulphate.

	Calculated for $C_{11}H_8ONCl$.	Found.
Cl	17.25	15.13

β-Naphthylformylchloramine (*Formylchloramino-β-naphthalene*), HCO—($NClC_{10}H_7$).—Adding an alcoholic solution of formyl-β-naphthalide, acidified with acetic acid, to a solution of calcium hypochlorite, gives a yellow precipitate, naphthylformylchloramine. It is easily soluble in chloroform, from which it is precipitated by ligroin. It is best recrystallized from hot ligroin (70° to 80°). The melting-point is 75°. It decomposes violently with an alcoholic solution of caustic potash.

0.1096 gram substance required 10.30 cc. N/10 thiosulphate.

	Calculated for $C_{11}H_8ONCl$.	Found.
Cl	17.25	17.26

β-Naphthylformylamine and Hypobromous Acid.—An alcoholic solution of formyl-β-naphthalide added to potassium hypobromite solution gave a yellow precipitate which, when crystallized from alcohol, melted at 164°. This compound was inactive toward potassium iodide, and on saponification, by heating an hour with 10 per cent potassium hydroxide,

gave a flaky, white compound containing bromine, and melting at 61° when recrystallized from water and from alcohol. This is probably 1-brom-2-aminonaphthalene (m. p. 63°), and if so, it shows that the bromine atom migrates easily to the ortho position in the aromatic ring. This is the usual reaction with all halogen aryl amides when the para position is occupied.

Varying the conditions of precipitation gave unpromising gums composed of some active nitrogen bromide and other bromine derivatives of formylnaphthalide, and no further attempts were made to isolate the compounds.

Formyl-α-naphthalide also gave unsatisfactory results when attempts were made to brominate it. An alcoholic solution of the naphthalide added to hypobromite solution gave an active yellow precipitate, which, however, was so unstable that, on filtering, it instantly became hot and charred.

α-Naphthylacetylchloramine (*Acetylchloramino-α-naphthalene*), $C_{10}H_7NCl$—CH_3CO.—An alcoholic solution of acetyl-α-naphthalide with a little acetic acid added to an excess of calcium hypochlorite solution gives, after a few minutes, a precipitate of the chlorine compound. It can be recrystallized from hot ligroin in fine, pure-white crystals, melting at 75°.

0.1150 gram substance required 10.24 cc. N/10 thiosulphate.

	Calculated for $C_{12}H_{10}NOCl$.	Found.
Cl	16.12	15.78

Halogen Derivatives of the Acyl Alkyl Amides.

Compounds of the type RCO—NHalR′, whether R is an alphyl or alkyl radical, are much more stable where R′ is an alkyl group than where it is an alphyl radical, because there is no tendency of the halogen atom to replace the hydrogen of an alkyl group as it does the hydrogen in an aromatic ring. It is possible, therefore, in such cases, and on trial it was found desirable, to attach chlorine to nitrogen by using the almost neutral solution made by dissolving chlorine in water instead of the usual alkaline calcium or sodium hypochlorite solution, or the acid solution obtained by acidifying these with weak acids such as acetic, carbonic, or boric. In this

case, as in the others, hypochlorous acid is still doubtless the reagent effecting the change, for Jawkowkin[1] has shown that chlorine water contains hypochlorous acid as well as hydrochloric.

To determine whether chlorine acts directly on the amides or only when in aqueous solution and, therefore, presumably hydrolyzed, 1 gram of ethylbenzamide was dissolved in chloroform with a few drops of potassium hydroxide solution and a stream of chlorine passed in for some time. On evaporating the solvent, the unchanged ethylbenzamide was recovered with no trace of an active nitrogen chloride.

Ethylbenzoylchloramine (Benzoylchloraminoethane),
C_6H_5CO—$(NClC_2H_5)$.—Ethylbenzoylchloramine may be made in the usual way by using hypochlorite solutions, but the best results were obtained by dropping a saturated solution of ethylbenzamide in alcohol into about ten times its volume of chlorine water, which must not be too cold but at about 10°. The oily drops may be made to crystallize by adding a crystal of ethylbenzoylchloramine, or, if there is none at hand, by heating a little of the mixture until it crystallizes on cooling and shaking, and then adding this to the mixture. More chlorine water may be used to give another crop. The compound is soluble in ether, alcohol, and hot water, and may be crystallized from the last in the form of very fine, white needles. The melting-point is 53°.5.

0.1540 gram substance required 16.8 cc. $N/10$ thiosulphate.

	Calculated for $C_{13}H_{10}ONCl$.	Found.
Cl	19.31	19.37

The stability of the compound is quite remarkable. It is not decomposed by boiling water, and it melts without change. Warming with ammonia water reduces it rapidly.

The corresponding chlorine derivative of metanitrobenzamide is not so easily prepared. Ethylnitrobenzamide was made by the action of metanitrobenzoyl chloride on ethylamine hydrochloride in the presence of an alkali. It can be recrystallized from hot water and melts at 120°. Attempts to

[1] Ztschr. phys. Chem., **29**, 613 (1899).

chlorinate this compound either by using hypochlorite solutions or chlorine water gave only traces of an active nitrogen halide.

Ethylbenzchloramide (1.8 grams) dissolved in alcohol was treated with potassium cyanide (0.7 gram). After warming for some time, the alcohol was distilled off, water added, and the solution extracted with ether. The ethereal solution gave only crystals of ethylbenzamide. On grinding together in a mortar ethylbenzoylchloramine (1.5 grams) with potassium cyanide (0.5 gram), the mixture became liquid and gave off a strong odor of hydrocyanic acid. In ten minutes the mass again became solid. It was extracted with ether which, on evaporation, gave crystals of ethylbenzamide, melting at 68° to 69°, so there were no other products in appreciable quantity. Therefore Berg's reaction does not take place under these conditions.

Ethylbenzoylchloramine (2 grams) was dissolved in dry ether, placed in the bottom of a tall cylinder filled with carbon dioxide, and a small glass bulb containing about 1 gram of zinc ethyl was dropped in. Although the solution was cooled to 0° the reaction was violent. On filtering and evaporating the solution, ethylbenzamide alone remained, having a melting-point of 66° without recrystallizing. There was, therefore, no evidence of any substitution of chlorine by ethyl.

Methylbenzoylchloramine (*Benzoylchloraminomethane*),
$(C_6H_5CO)NClCH_3$.—Methylbenzoylchloramine may be made by dissolving methylbenzamide in alcohol, dilute acetic acid, or water, and adding the solution to a solution of calcium hypochlorite or sodium hypochlorite, or simply to chlorine water. A saturated aqueous solution of the amide with chlorine water, both ice-cold, was found to give the best results. As the compound is somewhat soluble, it is usually necessary to extract with ether. Methylbenzoylchloramine is a colorless oil, heavier than water. It does not solidify at a temperature of —16°, even when inoculated with a crystal of ethylbenzoylchloramine. This substance was tried because it, too, was difficult to solidify, and because it was thought that the two compounds might be isomorphous.

0.2035 gram substance required 23.15 cc. N/10 thiosulphate.

	Calculated for C_7H_8ONCl.	Found.
Cl	20.9	20.2

Methylbenzoylchloramine is decomposed by boiling with water or with dilute potassium hydroxide solution, by a strong solution of potassium hydroxide in the cold, by heating alone, and on long standing in a desiccator. Methylbenzamide is formed in all these cases and Beckmann's rearrangement does not take place. A sample containing 15.7 per cent chlorine was heated on a water-bath for half an hour, and was then found to contain 14.2 per cent active chlorine. Yet in some cases, on the evaporation of its ethereal solution by an air-blast, it decomposed spontaneously with the production of much heat. It cannot be distilled without decomposition, even in a vacuum. Concentrated hydrochloric acid attacks it, giving off chlorine. Ammonia water decomposes it slowly, even in the cold, regenerating the amide.

The difference in stability between this compound and the homologous ethylbenzoylchloramine is very marked and the reagents which decompose the former completely have but very little effect on the latter. Evidently the ethyl group exercises a protecting influence over the halogen which is attached to the same nitrogen, which may be due to stereochemical causes.

Amylacetamide.—Amylacetamide was prepared by slowly mixing an ethereal solution of isoamylamine (2 molecules) with an ethereal solution of the calculated quantity of acetyl chloride (1 molecule). After adding water to dissolve the amylamine hydrochloride, the ether was evaporated and then the amylacetamide distilled at a temperature of 230° to 232°. It is an oil and forms a pale-yellow platinum salt when chlorplatinic acid is mixed with its alcoholic solution and ether is added.

Amylacetylchloramine (*Acetylchlor-4-amino-2-methylbutane*), CH_3CO—($NClC_5H_{11}$).—Adding isoamylacetamide to a solution of calcium hypochlorite gives the chlorine derivative as an oil, which, since it could not be distilled even in a vacuum

nor solidified in a freezing-mixture, could not be perfectly purified.

I. 0.3896 gram substance required 45.25 cc. N/10 thiosulphate.

II. 0.2552 gram substance required 30 cc. N/10 thiosulphate.

	Calculated for $C_7H_{14}ONCl$.	Found. I.	II.
Cl	21.66	20.48	20.85

This compound is remarkably stable. It was not completely decomposed on standing two days in acid or in ammonia solution, nor on being warmed with these. Boiling water, however, decomposes it explosively. It is miscible with glacial acetic acid and is not decomposed by it in the cold. It can be dissolved in acetic acid and reprecipitated by the addition of an alkali.

Amylacetylchloramine having been prepared by the action of hypochlorous acid on amylacetamide, the method of introducing the chlorine and the acetyl group in the reversed order was tried by acetylating amylchloramine, in order to prove that in compounds of this class the halogen is really held by the nitrogen atom (see page 291). Isoamylchloramine was prepared in a way similar to that used by Berg.[1] Ten grams of the amylamine hydrochloride were dissolved in water and added to 50 cc. of sodium hypochlorite solution containing 8 per cent active chlorine. The oil separates at once and can be dissolved in ligroin (35° to 40°), washed with water, and the ligroin evaporated off in a vacuum-desiccator. A manometer is used to indicate when the ligroin is expelled. The chloramine is extremely unstable, and unless quickly purified, it goes over spontaneously, and sometimes instantaneously, into amylamine hydrochloride and the dichloramine.

0.1428 gram substance required 23.51 cc. N/10 thiosulphate.

	Calculated for $C_5H_{12}NCl$.	Found.
Cl	29.17	29.20

[1] Bull. soc. chim., [3], **3**, 687 (1890).

This amylchloramine was added to a little more than its volume of acetic anhydride. The two do not mix when cold, but on allowing them to reach room temperature reaction takes place, producing a slight rise in temperature. Glacial acetic acid was then added, and afterwards water. The amyl-acetylchloramine separated from the solution and could be washed with water, or could be dissolved with ligroin or ether and washed and obtained by evaporating off the solvent. The colorless oil appears identical in all respects with that obtained by chlorinating the amylacetamide, and although it was not obtained absolutely pure, as it could not be distilled in a vacuum nor solidified, the results are sufficiently close to identify it.

I. 0.3961 gram substance required 46.02 cc. $N/10$ thiosulphate.

II. 0.1079 gram substance required 12.93 cc. $N/10$ thiosulphate.

III. 0.1012 gram substance required 11.85 cc. $N/10$ thiosulphate.

	Calculated for $C_7H_{14}ONCl$.	I.	Found. II.	III.
Cl	21.66	20.60	21.25	20.80

Considering the ease with which the acetylation takes place and the low temperature, it is not probable that any rearrangement occurs, and the reaction therefore affords conclusive evidence in favor of the formula $CH_3CO—NClC_5H_{11}$ as representing the constitution of this compound, and in favor of the corresponding structure for its analogues.

The Chlor- and Bromimido Ethers.

Ethylchlorimidobenzoate and Potassium Cyanide.—Ethyl-chlorimidobenzoate[1] does not react with potassium cyanide in absolute alcohol even on heating, but if water is added the reaction takes place spontaneously, potassium chloride crystallizes out, and the imido ether is regenerated. Eighteen grams of ethyl chlorimidobenzoate in aqueous alcohol were heated on a water-bath with 8 grams of potassium cyanide for an hour. After pouring the mixture into water, extracting with ligroin,

---

[1] Stieglitz: This JOURNAL, **18**, 755 (1896).

and distilling *in vacuo*, an oil was obtained which contained 9.15 per cent nitrogen.

0.1170 gram substance required 9.5 cc. N_2 at 23° and 739 mm.

	Calculated for $C_9H_{11}NO$.	Found.
N	9.41	9.15

The oil gave a slight reaction with potassium iodide and was therefore ethyl benzimido ether still containing a little of the unchanged chlorine compound. Berg's reaction does not, then, take place with the chlorimido ethers.

Ethyl chlorimidobenzoate and zinc ethyl give benzonitril as the chief product though a little ethylamine appears to be formed. Eight grams ethyl chlorimidobenzoate were dissolved in twice the volume of ether and added slowly to 5 grams of zinc ethyl, a reflux apparatus with a stream of carbon dioxide being used. The ether was distilled off and water added to the cooled residue. On acidifying the mixture with hydrochloric acid, a light oil separated which was extracted with ether and was proved to be benzonitril by dissolving it in alcohol with a little ammonium hydroxide and passing in hydrogen sulphide. The thiamide formed melted at 114°, and at 115° when mixed with some thiamide prepared from benzonitril for comparison. The benzonitril recovered weighed 4.2 grams, *i. e.*, 94 per cent of the theoretical yield.

The acid solution was made alkaline and distilled into hydrochloric acid in a Liebig bulb. On evaporation a very small amount of a salt was obtained which gave the isocyanide odor with caustic potash and chloroform. This showed the presence of a primary amine. An analysis of 0.0162 gram of the platinum salt gave 35 per cent Pt (calculated for $(C_2H_5NH_3)_2PtCl_6$, 39 per cent).

Ethyl Chlorimido-m-nitrobenzoate, $m\text{-}NO_2C_6H_4C(NCl)OC_2H_5$. —This compound is easily made by dropping the hydrochloride of nitrobenzimido ethyl ester into an excess of sodium or calcium hypochlorite solution warmed to about 30°. On cooling,

[1] Lossen: Ann. Chem. (Liebig), **265**, 144 (1891); Tafel and Enoch: Ber. d. chem. Ges., **23**, 1550 (1890).

the chlorine compound becomes solid and can be picked off the surface with a spatula and recrystallized from warm alcohol or ligroin. It can be separated from any unchanged material by repeated extraction with ligroin.

0.2128 gram substance required 18.63 cc. N/10 thiosulphate.

	Calculated for $C_9H_9N_2OCl$.	Found.
N	15.50	15.52

It crystallizes in stellar groups of slender white needles and melts at 61° without decomposition, but when heated a little above this temperature it suddenly heats up and boils. On heating cautiously 5.5 grams of the compound, not absolutely dry, to the temperature required for decomposition, the chief product was *m*-nitrobenzamide, with a small amount of ethyl *m*-nitrobenzoate. Both compounds were identified by mixing them with the synthetic preparations and taking the melting-points. No derivatives of nitraniline could be found.

It was thought that stereoisomers of this compound might be prepared, but all efforts to obtain these were in vain. For example, ethyl chlorimidonitrobenzoate was dissolved in ligroin and a very little dry hydrogen chloride passed in. The hydrochloride of nitrobenzimido ester was precipitated. Of the amount taken, 80 per cent was recovered.

Attempts were made to substitute the chlorine attached to the nitrogen atom of ethyl chlorimidonitrobenzoate by treating it with dimethylaniline with the hope of forming a derivative of *p*-aminodimethyl aniline,[1] but without success. The two compounds were heated together in alcohol, in strong oxalic acid solution, in dilute and in concentrated sulphuric acid, and without any solvent, but on testing the product in each case, after saponification in acid solution, with hydrogen sulphide and ferric chloride, there was no trace of methylene blue, and it must be concluded that dimethylphenylenediamine was not formed even in the minutest quantity. Treating the chlorine compound with *α*-naphthol and an alkali also gave no evidence of the substitution of chlorine by a radical.[1]

[1] The apparently analogous chlorimides of quinone react in this way with anilines and phenols.

On heating the nitrobenzchlorimido ester in absolute alcohol it is not changed, but if a trace of water is present the benzoate is produced.

Nitrobenzchlorimido ester differs decidedly from the chloramides in being so stable. Alkalies do not cause the Beckmann rearrangement, nor even decompose it. Heating the ester for half an hour on the water-bath with an excess of 10 per cent potassium hydroxide does not affect it.

Ethyl Bromimido-m-nitrobenzoate, $m\text{-}NO_2C_6H_4C(NBr)OC_2H_5$. —The hydrochloride of nitrobenzimido ethyl ester is added to a cold solution of potassium hypobromite and the solution filtered at once. The precipitate is treated with ligroin, which dissolves the bromine compound and leaves the unchanged hydrochloride. By evaporation of the ligroin the bromimide crystallizes out in fine white needles which melt at 71°, turn brown at 120°, and give off a gas at 130°.

0.0338 gram substance required 2.15 cc. N/10 thiosulphate.

	Calculated for $C_9H_9O_3N_2Br$.	Found.
Br	29.27	27.30

The substance melts under water without decomposition. Dilute hydrochloric acid gives off bromine, and ethyl nitrobenzoate is formed. As with the corresponding chlorine compound, the attempt to attach the nitrogen atom to a benzene ring was not successful. Heating the bromimide with dimethylaniline and then with concentrated and dilute sulphuric acid, and then treating with hydrogen sulphide and ferric chloride gave no methylene blue.

Ethyl Imidonitrobenzoate and Hypoiodous Acid.—Since the chlorine and bromine derivatives of *m*-nitrobenzimido ethyl ester were so stable, it was thought possible that the corresponding iodine derivative might be prepared in the same way. The imido ester was treated with iodine and then with a solution of potassium hydroxide and with crushed ice. In another experiment a hypoiodite solution, made by dissolving iodine in cold potassium hydroxide solution, was used, but although in all cases the ether or ligroin extract gave a minute residue of white or yellowish crystals from which dilute

hydrochloric acid set free iodine, yet the desired iodine body was not definitely proved to exist, and it can probably be obtained, if at all, only from reagents when water is entirely excluded.

Ethyl Chlorimido-β-naphthoate, β-$C_{10}H_7C(NCl)OC_2H_5$.—The naphthimido ethyl ester was made by dissolving 15 grams of β-naphthonitril in 75 grams of ether and 8 grams of absolute alcohol, and passing in 10 grams of dry hydrogen chloride. The imido ester hydrochloride crystallizes out, on long standing, in plates. It decomposes with effervescence at 135° and forms the amide (m. p. 192°). Calcium hypochlorite solution has little effect on it in the cold, but if the solution is first heated to 60° or 70° the chlorine compound is readily formed, and can be filtered off on cooling and recrystallized from hot ligroin in beautiful stellar groups of needles and plates. It is very soluble in ether, from which it crystallizes in small, round nodules.

0.0525 gram substance required 4.48 cc. N/10 thiosulphate.

	Calculated for $C_{13}H_{12}ONCl$.	Found.
Cl	15.12	15.13

The chlorimidoester melts at 71° without decomposition, and only at 185° does it give off a gas with an agreeable odor, which burns with a green flame (ethyl chloride?). A gummy mass is left.

Ethyl chlorimido-β-naphthoate is not decomposed even by boiling with strong ammonium hydroxide. With sodium methylate it reverts to the nitril. On heating 1.5 grams with 10 cc. of anhydrous methyl alcohol containing sodium methylate prepared from 0.3 gram sodium, it reacted at once, the imido ether melting and dissolving. On pouring the mixture into cold water, naphthonitril was precipitated. Recrystallized from ligroin it melted at 66°, even when mixed with naphthonitril.

Berg's reaction does not take place with naphthchlorimide ester. Five grams of imido ester with one gram of potassium cyanide in absolute alcohol were warmed for half an hour on the water-bath. Most of the alcohol was then distilled off and

the residue extracted with ether. The part soluble in ether was distilled and found to be naphthonitril (m. p. 66°). The portion insoluble in ether (mostly potassium chloride) was dissolved in boiling water and some naphthoic acid crystallized out on cooling (m. p. 182°).

To 6 grams of the chlorimide in absolute ether were added 2.15 grams of zinc ethyl. There was no reaction at 0°, but when the mixture was allowed to come to the temperature of the room a slow effervescence began and continued for several hours. Filtering off the ether and evaporating it gave naphthonitril. On repeating the experiment with 20 grams of the chlorimide and 5.4 grams of zinc ethyl, there was a more rapid effervescence, but no precipitation of a zinc compound. On evaporating the solution in a vacuum, a salve-like mass was left which, treated with water, gave over 200 cc. of gas. The residue was extracted with ether and evaporated. A small portion of the product was recrystallized from ligroin and proved to be naphthonitril. In order to detect the presence of an amine, even in minute quantity, the remainder of the product was digested with sulphuric acid of varying concentration on a water-bath for several days. On pouring the solution into water, filtering off the unchanged nitril, making the filtrate alkaline with sodium hydroxide, and extracting it with ether, there was no evidence of an amine, from which it appears that zinc ethyl does not substitute ethyl for chlorine in acting on the chlorimide.

Ethyl Bromimido-β-Naphthoate, β-$C_{10}H_7C(NBr)OC_2H_5$.— This compound is made in the same way as the corresponding chlorine compound and resembles it in crystalline form and solubilities. Melting-point, 76°.5 to 77°.

0.1812 gram substance required 5.83 cc. N/10 thiosulphate.

	Calculated for $C_{13}H_{12}NOBr$.	Found.
Br	28.74	28.70

It crystallized from warm ligroin in pure white needles. It is remarkably stable. Boiling water and even sodium hydroxide solution attack it only very slowly. Standing over

night with strong ammonium hydroxide does not decompose it.

To Professor Stieglitz, not only for his skill in directing this work but also for his patience and kindness toward me personally, I feel very grateful.

THE RED AND THE YELLOW MERCURIC OXIDES AND THE MERCURIC OXYCHLORIDES.[1]

By Eugene P. Schoch.

According to Millon,[2] Roucher,[3] and Thümmel[4] the different mercuric oxychlorides exist in several isomeric modifications. It is stated that some of the isomers, on treatment with sodium hydroxide solution, give yellow mercuric oxide while the others give red. This would seem to indicate that there are two series of compounds, one of which is directly related to the yellow oxide, and the other to the red oxide. The two oxides, then, should be essentially different. Yet the results of recent investigations of the relations between the oxides contradict this conclusion. Since the published accounts of the several investigators of the oxychlorides are at variance on many points of detail, it seemed desirable to repeat critically all the methods of preparation of the oxychlorides, and to test the properties of these bodies with special reference to determining what oxide each yields when treated with sodium hydroxide solution. This problem was suggested to me by Professor Felix Lengfeld, formerly of the University of Chicago, and the work in this paper has been carried out under his direction.

It is evident that the solution of this problem requires a comparative study of the mercuric oxides. Hence, this paper is divided into two parts, presenting :

(1) A Study of the Mercuric Oxides.

(2) The Preparation and Properties of the Oxychlorides.

[2] Ann. chim. phys., (3), **18**, 372.

[3] *Ibid.*, (3), **27**, 353.

[4] Arch. Pharm., **227**, 589.

PART I.

A STUDY OF THE MERCURIC OXIDES.

It is well known that the red oxide of mercury, as ordinarily prepared by heating mercuric nitrate, is crystalline in its structure. Determinations of its crystal form were made by Nordenskjöld,[1] and by Descloizeaux,[2] who found that the crystals belonged to the monoclinic system. The structure of the yellow oxide, however, was an open question. Pelouze[3] and Millon[4] both state that it is amorphous, but beyond Millon's observation that under the microscope the yellow oxide presents the appearance of rounded globules, there is no record that either investigator subjected this substance to a critical examination. They considered the oxides as essentially different on account of the following differences in behavior. Pelouze points out that chlorine acts very slightly on the red oxide while it acts readily on the yellow oxide. Millon notes that the yellow oxide is converted by oxalic acid solution to white oxalate of mercury, and by alcoholic mercuric chloride solution to the black oxychloride, $HgCl_2,2HgO$, while the red oxide is scarcely affected by either reagent. Both authors admit that all of these differences are quantitative rather than qualitative. It is easily found by trial that the differences become less and less as the red oxide is more finely powdered. Concerning the action of oxalic acid, this conclusion has been confirmed recently by Koster and Stork.[5] Hence these differences in the behavior of the two oxides pointed out by Millon and Roucher do not appear to give ground enough whereon to base the conclusion that the oxides are essentially different.

In contrast to the older idea, that the yellow oxide is amorphous, are the results of recent investigations which seemed to show that the two oxides are identical and differ only in the size of the particles. Ostwald[6] found that both

[1] Pogg. Ann., 114, 612.
[2] Ann. chim. phys., (4), 20, 210.
[3] Compt. rend., 16, 50.
[4] *Loc. cit.*
[5] Rec. trav. chim. Pays-Bas., 20, 394.
[6] Ztschr. phys. Chem., 18, 159.

oxides have very nearly the same solubility in normal solutions of potassium bromide, potassium iodide, and of sodium thiosulphate, and that a cell "mercury-yellow oxide-potassium hydroxide solution-red oxide-mercury" gave no appreciable electromotive force. This latter would show that the two oxides have the same solubility. However, Cohen[1] measured the electromotive force of a cell arranged in the same way with a much more delicate electrometer, and concluded from his results that at ordinary temperatures the yellow oxide is more soluble than the red and hence, that they could not be identical. In answer to this, Ostwald[2] showed that the solubility of a sparingly soluble powder varies appreciably with the size of the particles, a fact which has received further confirmation by Hulett,[3] and appears to have a secure theoretical foundation. By grinding red oxide of mercury very fine, Ostwald found that its solubility in normal potassium bromide and the other solutions referred to can be made equal to the solubility of the yellow oxide, and even to exceed it. He concludes that the two oxides are identical.

With the exception of some bare statements to the effect that the yellow oxide, on heating, changes to the red,[4] and that it dissociates at a lower temperature,[5] the foregoing is all that has come to my notice which in any way bears on the subject.

My own results may be summarized as follows :

(*a*) Yellow oxide, when precipitated, washed, and dried at the ordinary temperature, is crystalline, but shows a form entirely different from that in which the red oxide crystallizes. Under a microscope which magnifies 1,000 to 1,200 diameters the yellow oxide is seen to be in the form of square tablets.

(*b*) The crystals of the yellow oxide grow when allowed to remain, at the ordinary temperature, in contact with the precipitation mixture, or with sodium or potassium chloride solutions. At the same time the color of the mass changes from a pale-yellow to an orange, and after some weeks to a decidedly

[1] Ztschr. phys. Chem., **34,** 69.

[2] *Ibid.,* **34,** 495.

[3] *Ibid.,* **37,** 385.

[4] Carnelley and Walker : J. Chem Soc. (London), **53,** 59.

[5] Wallace : Chem. Gaz., 1858, p. 345.

reddish tint. It appears from this that the square tablets are stable at the ordinary temperature.

(*c*) When the crystals of the yellow oxide are boiled in aqueous solutions of salts, they change to the prismatic form of red oxide. The change takes place very completely when a little of the powder is suspended in a 10 per cent (or stronger) solution of sodium or potassium bromide or chloride and the mixture boiled for an hour. The color of the resulting mass may or may not be deeper, depending upon the relative sizes of the crystals before and after change. Samples precipitated hot show a number of prismatic crystals.

(*d*) On heating dry samples of the yellow oxide to temperatures from 250° C. to 600° C., for periods of eight to twenty-four hours, the crystals changed to the prismatic forms of the red. In this connection it was found that yellow oxide changed in color to a deep-orange or yellowish-red, while samples of red oxide which had been ground fine till they were yellow in appearance, did not change, although heated to the same temperature and for the same length of time. The microscope revealed the fact that the samples of red oxide were still made up of the same fragments of prismatic crystals of which they consisted before heating, while the samples of yellow oxide showed a complete change of form to the prismatic.

It is evident that, to some extent, the color of the mass does not enable us to decide whether a sample is the yellow or the red oxide. I have obtained samples with square tabular crystals (yellow) that show a deeper color than many samples with prismatic crystals (red).

(*e*) The prismatic crystals obtained according to (*c*) and (*d*) are identical with the regular red oxide crystals. Miss H. Whitten, of the University of Texas, examined these samples and gave me the following statement of her conclusion. "All show decidedly prismatic forms, singly, or in aggregates. From the appearance of prism and pinacoidal faces shown by all the forms examined, I would say they are typical monoclinic prisms. $<\beta$ was not (could not be) measured, but appeared constant in all the samples."

It appears, then, that mercuric oxide exists in two crystalline forms : one, square tabular crystals, is formed by precipitation at the ordinary temperature, and changes to the other form when exposed to higher temperatures ; the other, monoclinic prisms, results in all preparations made at temperatures above the ordinary.

In considering the question of their relation, the first possibility that presents itself is that the yellow oxide is an hydroxide. Though this point had been carefully investigated by Siewert,[1] it appeared desirable to study it again, because Carnelley and Walker[2] announced a contrary result. The experimental results, given elsewhere, agree perfectly with Siewert's and show that the yellow oxide is not a hydrate and that the two oxides have the same composition.

Different crystal forms of the same substance usually have different densities, and since no record of determinations of the density of the yellow oxide could be found, comparative determinations with both oxides were made. However, it soon became evident that the difference in density, if any exists, is very small. The amount of time necessary for accurate density determinations rendered it undesirable to continue this work at that time.

Since at higher temperatures the yellow oxide changes to the red, the dissociation pressure of the yellow should be greater than that of the red. This has been found to be the case. At 300° to 320° C. the dissociation pressure of the yellow is 760 mm. and over, while that of the most finely powdered red oxide does not exceed 400 mm. Of course, the yellow oxide is soon converted to the red. After an hour's heating at 380° the yellow exerted a much smaller tension—one corresponding to the red.

Other relations between the oxides, such as solubility, relation of specific heats, etc., have not been studied so far, but are to be determined by future work. It is probable that the solubility of the yellow oxide at and below the ordinary temperature is less than that of the red oxide, the size of the particles of both samples being the same. This is to be expected from

[1] Ann. Chem. (Liebig), **125**, 226.
[2] *Loc. cit.*

the fact that the crystals of the yellow became larger, as shown in (*b*) above, and also from the fact found by Ostwald that the solubility, in normal potassium bromide solution, of red oxide finely ground with garnets exceeded that of the yellow oxide.

Furthermore, it follows that at low temperatures the prismatic crystals should change to the square, tabular, and that there should be a definite transition temperature for these two forms.

In the light of the information just presented the oxides obtained by treating the mercuric oxychlorides with sodium hydroxide present nothing new or peculiar. I found that all the ten oxychlorides I have prepared (see second part of this paper) when treated with sodium hydroxide at the ordinary temperature, yield an oxide that contains square tabular crystals. In some cases the form was not well defined, but it certainly was not prismatic. However, when it became necessary to heat the mixture in order to decompose the oxychloride thoroughly (*e. g.*, black trimercurdioxychloride) prismatic crystals were obtained. These results agree perfectly with the preceding.

It is probable that Millon, Roucher, and Thümmel took the colors of the masses as a criterion. I have already pointed out that the color does not enable us to decide, and I found my view corroborated in this case : the difference in the colors of the oxides obtained from the oxychlorides is due to the sizes and irregularities of the particles, and in some cases, to the presence of nuclei of undecomposed oxychloride.

Preparation of Mercuric Oxide Showing Square Tabular Crystals.

Cold saturated mercuric chloride solution was added to sodium hydroxide solutions of concentrations ranging from 2 to 30 per cent. The ratio between the amounts of mercuric chloride and sodium hydroxide never exceeded that of 1 molecule of mercuric chloride to 10 of sodium hydroxide. For the most concentrated sodium hydroxide solutions the relative quantity of mercuric chloride added was much less ; the quan-

tities were in the ratio of 1 molecule of mercuric chloride to 20 of sodium hydroxide. The addition of more mercuric chloride solution would have made the mixtures too dilute. The mixtures were allowed to stand from four to six weeks with occasional stirring. In all except the most concentrated, the yellow precipitates soon turned orange, the color deepening day by day for about two weeks. The maximum change was observed with the 10 per cent sodium hydroxide mixture, a deep orange or reddish-yellow color being produced.

Some precipitates, prepared as above, were washed by decantation immediately after precipitation, while they were still pale-yellow, and then they were allowed to stand, part under pure water, part under 10 per cent sodium hydroxide solution. No perceptible change took place. When sodium chloride was added to the solution the change began.

After four to six weeks, the precipitates were washed, dried, and examined under the microscope. The following description, based upon an examination of ten samples, was given me by Mr. R. D. George, of the Department of Geology of the University of Chicago :

"The samples show a considerable number of small tabular crystals of apparently equal lateral axis. The exact outline of the crystals could not be determined on account of the light interference. In polarized light the crystals showed distinct double refraction, giving a pale yellowish-green interference color. The existence of double refraction was further confirmed by the use of the selenite plate."

"Besides these small crystals there were others of larger size, having angles differing by a few degrees from a right angle. These presented the appearance of skeleton crystals. The centers presented much less obstruction to the passage of light than the borders did. The shape of the less opaque central part could not be determined, but its outline appeared rounded and not parallel with that of the ¦crystal as a whole. This apparent difference of form may have resulted from light interference, or from the presence of a greater thickness of the crystal substance at the angles."

From the microscopic examination it also follows that the

change in color noted above was due to an enlargement of the crystal grains. This probably takes place as usual : the smaller grains dissolve and the oxide crystallizes out again on the surface of the larger crystals. Hence, anything that increases the solubility of the mercuric oxides hastens the change. In accordance with this I found that water or sodium hydroxide solution free from chloride had no perceptible effect, while on the addition of sodium chloride to both a change in color was immediately noticed. As is well known, mercuric oxide is but very slightly soluble in water, and probably not much more soluble in sodium hydroxide solution, but it is much more soluble in solutions of many salts. While I tried sodium and potassium chloride only, it is to be expected that other salts, such as sodium nitrate or sulphate, would have a somewhat similar effect.

Experiments Showing that the Crystals Obtained by the Action of Hot Aqueous Solutions on Yellow Mercuric Oxide are Prismatic.

1. One hundred cc. of hot mercuric chloride solution (50 grams of mercuric chloride to 100 cc. water) were added, gradually, to 500 cc. of hot potassium hydroxide solution (50 grams of potassium hydroxide to 100 cc. water). The mixture was boiled for five hours in a flask with a reflux condenser. Then the precipitate was allowed to settle, was washed by decantation, and finally spread on porous plates to dry. The microscopic examination showed that most of the particles were in the form of prismatic crystals. Other forms could not be clearly recognized.

2. An excess of hot potassium hydroxide solution was added to 250 cc. of hot mercuric chloride solution, both of the same concentrations as in 1. The mixture was boiled for five hours in a flask with a reflux condenser, then the precipitate was washed and dried. The mass did not show any well defined crystals of any sort. It should be noted, in passing, that the quantity of precipitate relative to the same volume of solution was at least six times as large in this case as in number 1. This may account for the absence of well formed crystals.

3. Mercuric oxide was prepared by Bosetti's[1] method, adding hot barium hydroxide solution to a hot concentrated mercuric chloride solution. The oxide obtained showed some well-defined, prismatic crystals, though on the whole it was decidedly impure.

4. One hundred grams of yellow oxide were suspended in 500 cc. of potassium hydroxide solution (same concentration as before) and the mixture boiled for five hours. The oxide was then washed and dried. Under the microscope prismatic crystals could not be clearly identified.

5. Thirty-five grams of the yellow oxide as in 4 were boiled for five hours in a solution of 125 grams of potassium chloride, 125 grams of potassium hydroxide, and 400 cc. of water. The oxide was then washed, dried, and examined. It was made up of well-formed, prismatic crystals.

6. Twenty grams of the same sample of yellow oxide were boiled for two hours in a solution of 220 grams of potassium chloride in 500 cc. of water previously saturated with mercuric oxide. On examination this sample showed large prismatic crystals.

Experiments 1 to 3 differ from the others in this respect : the oxide was first formed in the mixture, while in experiments 4 to 6 yellow oxide was added as such.

The same considerations which suggested themselves in connection with the enlargement of the crystal grain of the yellow oxide find application here. The largest and most perfect crystals were obtained by the action of the solution which dissolved the largest amount of the oxide. In experiments 2 and 4 prismatic crystals were not formed, probably because in 2 the volume of the solution was inadequate and in 4 the solubility of the oxide was slight.

Determination of Water in the Yellow Oxide.

Siewert[2] had found that yellow mercuric oxide, dried carefully over sulphuric acid, contained only 0.52 per cent of water as obtained by absorption in a calcium chloride tube. Carnelley and Walker merely heated mercuric oxide (air-

[1] Pharm. Ztg., **35**, 471.
[2] *Loc. cit.*

dried for five months) in a crucible and determined the loss in weight at different temperatures. They found a loss of 0.50 per cent up to 100° C. and 8.5 per cent up to 175°. At this temperature they report complete dehydration, and, at temperatures beyond these, incipient decomposition. The grounds for deciding that up to this point there is dehydration and not decomposition are not clearly stated : perhaps they thought decomposition could not be extensive since, according to Myers, the dissociation pressure of mercuric oxide at 175° is very low. However, I had observed that yellow mercuric oxide decomposes appreciably at that temperature, hence I thought that the loss due to heating the oxide above 100° may be due entirely to decomposition.

Yellow oxide was freshly prepared from mercuric chloride with an excess of sodium hydroxide, samples (a) and (b), by pouring the hydroxide into the chloride solutions ; sample (c) by reversing the procedure. The samples were washed nine times by decantation with large quantities of water, and were tested for chlorine by dissolving them in nitric acid, precipitating the mercury as the sulphide, boiling the filtrate till free from hydrogen sulphide, and adding silver nitrate. Chlorine was absent. They were dried in a vacuum desiccator for four days.

The samples were heated in an air-bath at 80° for four hours, to constant weight.

(a) 10.7447 grams lost 0.0370 = 0.34 per cent.
(b) 20.0900 " " 0.0500 = 0.24 "
(c) 21.0526 " " 0.0568 = 0.27 "

These samples were then placed in U-tubes, through which was passed a slow current of dry air. The tubes were heated in a bath of concentrated sulphuric acid. The upper parts of the U-tubes were kept cool. The current of air was drawn through calcium chloride absorption tubes. The bath was gradually heated up to 198° in the course of four hours.

(a) 10.7143 grams lost 0.0257 gram = 0.23 per cent ; its calcium chloride tube gained 0.0371 gram = 0.34 per cent.

(b) 11.3273 grams lost 0.0121 gram = 0.16 per cent ; its calcium chloride tube gained 0.0273 gram = 0.24 per cent.

(*c*) 10.8265 grams lost 0.0217 gram = 0.20 per cent ; its calcium chloride tube gained 0.0356 gram = 0.33 per cent.

Considerable decomposition had taken place in all the samples, as shown by the mercury deposited in the cool parts of the Ա-tubes. To determine the amount, another portion of sample (*c*) was heated in a dish in an air-bath to 175° for three hours—10.0216 grams lost 0.8117 gram = 8.1 per cent.

Two other samples prepared as above were analyzed for mercury by electrolysis.

I. 0.4019 gram substance gave 0.37135 gram Hg.

II. 0.36985 gram substance gave 0.34125 gram Hg.

	Calculated for HgO.	Found. I.	II.
Hg	92.6	92.4	92.3

An average of about 0.50 per cent of water was found in the yellow oxide, agreeing with Siewert's result. The hydrate $Hg(OH)_2$ requires 7.68 per cent. The loss in weight that Carnelley and Walker report as water was most likely due to decomposition.

Determination of the Densities of the Oxides.

The densities were determined in absolute alcohol, and the temperature noted to 0°.1. The air was removed by placing the flask containing the oxide with enough alcohol to cover it, in a vacuum desiccator ; under low pressure the alcohol boiled at the ordinary temperature, thus aiding the removal of the air. No constant temperature room and similar refinements were employed, hence the experimental error is relatively large, especially with substances of such great density.

Red oxide, Kahlbaum	27°.5	11.08
Same, finely ground	27°.5	11.11
Yellow oxide, my own preparation	27°.5	11.03
Yellow oxide, Kahlbaum	28°.5	11.08

Determination of Dissociation Tension.

In attempting to measure the dissociation tension of the mercuric oxides, one is confronted by a peculiar difficulty : since the manometer with which the apparatus is connected must be kept cool, the mercury condenses at this point, and

constantly disappears from the vapor in the hot part of the
apparatus.   I soon found by trial that equilibrium cannot be
maintained even for ten or fifteen minutes unless the distilling
of the mercury is prevented or minimized.   After trying
various forms of apparatus, I found the following to work sat-
isfactorily (see sketch) : The oxide was put into a tube 1 cm.
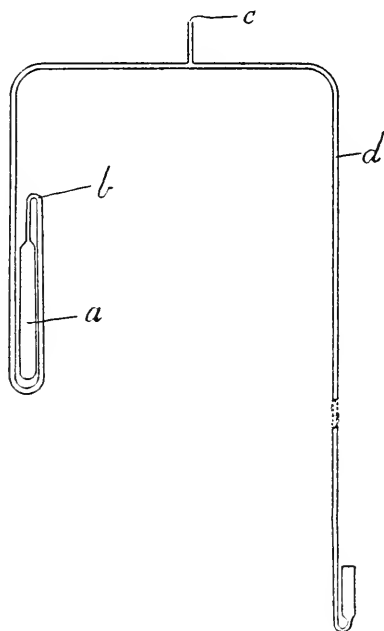
in diameter and 20 cm. in length, closed at its lower end and
at the upper fused to a capillary tube about 1 mm. in diame-
ter.   This capillary tube was bent 10 cm. from the joint so
that it extended downward close to the wide tube.   Then it
was bent to pass around the lower end and up along the tube
again.   Finally, 10 cm. above the first bend it was bent at a
right angle and extended out some 30 cm. from the heating
oven, where the tube was bent downwards to serve as a man-
ometer. The wide tube with the capillary tube around it was
placed as deep into a well-closed air-bath as the exit tube
would permit.   By this means the distillation of the mercury

was retarded so that equilibrium was not sensibly disturbed by this cause. In testing the apparatus I found that a sample of red oxide kept at 400° for two hours did not vary more than 3 to 5 mm. from its mean pressure (182 mm.). At the end of the time it registered 184 mm.

The manometer consisted of a continuation of the capillary tube 32 inches in length, to the lower end of which was fused a short piece of wide tubing, bent upwards, to serve as a reservoir for mercury. This reservoir was open to the air, and, from it, the mercury was drawn into the manometer tube as the apparatus was exhausted.

In every case the manometer was filled so as to avoid air bubbles on the tube, all the moisture was carefully removed from the apparatus, and the air exhausted to 1 mm. or less, as measured by another manometer on the pump.

The samples were dried for four days in a vacuum desiccator over phosphorus pentoxide. To insure the absence of mercurous oxide, the samples were heated above 100° by means of a boiling salt solution (b. p. 108°) while the apparatus was being exhausted (ten to fifteen minutes). Twenty to twenty-five grams of oxide were placed in each apparatus.

Trial experiments showed that the ground red oxide exerts a greater tension than the coarse oxide, hence, I used finely ground red oxide in comparing its tension with that of yellow oxide.

I had also found that yellow oxide shows its own proper tension only for a very short time when first heated. For instance, a sample of Kahlbaum's yellow oxide, when first heated to 320°, showed a pressure of 660 mm. It was then allowed to cool, having been hot for less than two hours altogether. Then it was shaken up, exhausted again, and heated to 350°, when it showed a tension of 200 mm., while a sample of coarse red oxide heated with it showed a tension of 160 mm. Hence I decided to heat the samples rapidly to a certain temperature and to take the first reading that the yellow oxide gives.

For the final trial the following samples were heated together :

1. Red oxide, finely ground.
2. Merck's best yellow oxide.
3. Yellow oxide, my own preparation, well crystallized.

These were heated rapidly to 310°. All samples reached their maximum pressures quickly. Number 3 exerted a pressure of 760 mm., and evolved several bubbles of gas through the manometer. Number 2 exerted a pressure of 730 mm., and, after half an hour, showed a slight decrease of 10 to 15 mm. No 1 soon reached 370 mm. and after an hour stood at 375 mm.

PART II.

PREPARATION AND PROPERTIES OF THE OXYCHLORIDES OF MERCURY.

There are three distinct methods of preparing oxychlorides of mercury :

(1) By the action of alkali bicarbonates on mercuric chloride solutions.

(2) By the action of mercuric oxide, red or yellow, on mercuric chloride solutions.

(3) By the fusion of mercuric oxide with mercuric chloride.

The first method was studied by Millon.[1] His work is both accurate and exhaustive, and little of note has been added since.

Roucher[2] investigated the second method. Many of the compounds he reported were afterwards found to be mixtures.

Thümmel[3] repeated the work of both Millon and Roucher. He revised the latter's results and gave definite directions for the preparation of all known oxychlorides by wet methods. In preparing my own samples, I subjected Thümmel's directions to a critical review, and found them correct with the exception of the modifications and differences presented farther on.

The third method is given by André.[4] He fused together

[1] *Loc. cit.*
[2] *Loc. cit.*
[3] *Loc. cit.*
[4] *Loc. cit.*

mercuric oxide and mercuric chloride in nearly stoichiometric proportions. Unlike Thümmel's directions, André's could not be depended upon. He claims to have prepared four oxychlorides, but probably none were pure, and hence the whole method was submitted to investigation.

I propose to name the oxychlorides by indicating the number of mercury and oxygen atoms, thus :

> $2HgCl_2,HgO$, trimercuroxychloride ;
>
> $HgCl_2,2HgO$, trimercurdioxychloride, etc.

I obtained ten oxychlorides, one $2HgCl_2,HgO$, trimercuroxychloride, and three isomers of each of the following :

> $HgCl_2,2HgO$, trimercurdioxychloride ;
>
> $HgCl_2,3HgO$, tetramercurtrioxychloride ;
>
> $HgCl_2,4HgO$, pentamercurtetroxychloride.

Dimercuroxychloride, $HgCl_2,HgO$, could not be obtained.

All the compounds were analyzed. For the determination of chlorine two methods were employed. In one the substance was heated with pure calcium oxide in a piece of combustion tubing to expel the mercury. The mass was dissolved in dilute nitric acid, and the chlorine determined as usual. This was tested by five check analyses, agreeing within 0.2 per cent. In the second method, the oxychloride was dissolved in acetic acid, and a solution of 10 grams of sodium acetate with an excess of silver nitrate added, the mixture heated to 70° with stirring, and then allowed to cool in the dark. Two trial determinations agreed to 0.1 per cent. The mercury was determined by electrolysis.

I determined the densities of all the oxychlorides, proceeding as for the oxides (see page 329).

I will discuss individually the oxychlorides prepared by wet methods as far as I have noticed anything new about them, and afterwards present an investigation of the fusion of mercuric chloride with mercuric oxide.

Trimercuroxychloride, $2HgCl_2,HgO$.—For the preparation of this substance Thümmel's directions were inadequate. An absolutely pure sample of this substance could not be obtained

by using red oxide or commercial samples of yellow oxide, even with the following procedure, though this yielded better results than any other : A sample of red and another of commercial yellow oxide were moistened, ground in a mortar, and added slowly, with stirring, to moist mercuric chloride (1 part of oxide to 10 of chloride and 5 of water). The masses were put in glass-stoppered bottles and shaken for four days in a thermostat at 65°. The substances still showed particles of unconverted oxide, and were easily decomposed by the light. The analysis of a sample prepared from red oxide showed 18.01 per cent chlorine ; that from commercial yellow oxide 18.2 per cent (theory, 18.69 per cent).

However, a pure sample was obtained by using moist yellow oxide freshly precipitated at the ordinary temperature. This was added gradually to moist mercuric chloride in the proportions given above. The mixture was warmed in a water-bath with occasional stirring, the liquid decanted, the mass dried, and then washed with absolute ether to remove all excess of mercuric chloride. This compound has a pale straw-yellow color.

I. 0.5242 gram substance gave 0.3901 gram AgCl.
II. 0.5278 gram substance gave 0.3969 gram AgCl.

	Calculated for $2HgCl_2.HgO.$	Found. I.	II.
Cl	18.69	18.4	18.56

Another method that yielded a pure compound was the following : 25 to 30 grams of mercuric chloride were dissolved in 100 cc. of boiling water and as much finely ground mercuric oxide was added as the solution would dissolve. The mixture was then cooled and the crystals separating between 60° and 40° were collected, dried, and washed with ether. The samples showed relatively large crystals of isometric rhombic dodecahedra.

0.4526 gram substance gave 0.3376 gram AgCl.
0.4718 gram substance gave 0.3738 gram Hg.

	Calculated for $2HgCl_2.HgO.$	Found.
Cl	18.69	18.47
Hg	79.20	79.00

Roucher claimed that among the crystals separated below 40° a less basic oxychloride can be found, but I noted nothing that would indicate the existence of such a compound.

I found the density of trimercuroxychloride to be 6.42.

Trimercurdioxychloride, $HgCl_2,2HgO$.—The red and the black modifications of trimercurdioxychloride are perhaps the most interesting of these bodies, because they, more than any of the other oxychlorides, present clearly a case of isomerism, which is otherwise so rare among inorganic compounds. The two sets of crystals have different densities, and show a notably different behavior with reagents. For example, both alkali carbonate and alkali chloride solutions readily act upon the red modification in the cold, while they do not affect the black even on boiling.

I made a comparative study of the methods of preparation of these isomers, and noted that the conditions for the formation of these compounds are essentially identical, except that for the preparation of the red modification the liquid must be slightly acid, while for the black it must be slightly alkaline. This may be seen from the following statement of facts.

Under the following conditions only the black modification is formed :

(*a*) By the action of sodium acetate on mercuric chloride solution.[1] The mixture has an alkaline reaction towards litmus. Black trimercurdioxychloride crystallizes out very slowly.

(*b*) By the addition of very small quantities of potassium bicarbonate solution, at intervals of half a day or a day, to mercuric chloride solution. The amount of the potassium bicarbonate added should be so slight that no precipitate will be produced. As the carbon dioxide escapes, and the solution becomes faintly alkaline, black trimercurdioxychloride crystallizes out slowly.

(*c*) By shaking an excess of mercuric oxide with a very dilute solution of mercuric chloride. Here the liquid is under the predominating influence of the mercuric oxide. This latter is an essential point, and may be noted again when mer-

[1] Volhard : Ann. Chem. (Liebig), **255**, 252.

curic chloride is poured upon a thick layer of mercuric oxide without disturbing the latter, and the whole allowed to remain at rest.   Black trimercurdioxychloride does not form in the top layer of the oxide, but forms in lower layers.

(*d*) By the action of water on trimercuroxychloride.

The method usually employed to obtain the black trimercurdioxychloride in larger quantity—adding mercuric oxide gradually to a boiling solution of mercuric chloride—probably depends on the action shown in (*d*) and is complicated by the fact that the oxide and chloride first form trimercuroxychloride.

Under the following conditions only the red modification is formed :

(*e*) By the action of marble on mercuric chloride solution.[1] The oxychloride forms on the bottom and the sides of the vessel—not on the marble.   The solution is faintly acid to litmus.

(*f*) By mixing solutions of mercuric chloride and potassium bicarbonate, in the proportion of 8 molecules of mercuric chloride to 11 molecules of potassium bicarbonate.   At the beginning the mixture is alkaline, and the action results in the formation of a yellow oxychloride—probably tetramercurtrioxychloride, which is more basic than the one under discussion—but the alkalinity is soon overcome by the acid liberated, and now the red trimercurdioxychloride is formed.   Of course, carbonic acid escapes in large amount, and in the end the liquid is alkaline, because in the equilibrium condition of potassium chloride and mercuric oxide the liquid must be alkaline.

(*g*) By the addition of alcohol to mercuric chloride solutions which have been treated with mercuric oxide.   In this case the solution is acid to litmus.

Methods (*a*) and (*b*) for the black are comparable to (*e*) and (*f*) for the red compound, and (*c*) is comparable to (*g*). All of these support my observations that the only difference in the preparation of these isomers is the acidity or alkalinity of the liquid.   There is no method for the red corresponding to method (*d*) for the black compound.

[1] Arctowski : Ztschr. anorg. Chem., **9**, 178.

Thümmel converted the red into the black oxychloride by heating: I could not bring about this conversion by any means. As I obtained the red it does not form square plates, as Thümmel found, but short hexagonal prisms (almost plates) with a pyramid on each end.

I found the density of the red modification to be 8.16 and that of the black 8.53.

Tetramercurtrioxychloride, $HgCl_2,3HgO$.—This, like the preceding, cannot be obtained pure by following Thümmel's directions, that is, using red oxide or commercial yellow oxide of mercury, even when prepared by grinding the oxides moist, adding them to the mercuric chloride in cylinders, and mixing by slowly inverting the cylinders again and again for several hours. When thus prepared, a sample from the red oxide showed 7.58 per cent chlorine, and one from the yellow 7.63 per cent. This seems to be sufficiently near the per cent required by theory (7.7 per cent), but even the trace of oxide in these samples renders the preparation unstable. The compound is obtained pure by using freshly precipitated oxide and adding it to cold saturated mercuric chloride solution so that the relative quantities do not exceed the proportion of 2 molecules of mercuric chloride to 1 molecule of mercuric oxide. The mixture is gently shaken after each addition. After standing about ten minutes the liquid is decanted, the mass dried on porous plates, and then washed with absolute ether.

    I. 0.4216 gram substance gave 0.1326 gram AgCl.

    II. 0.5823 gram substance gave 0.1818 gram AgCl.

    III. 0.3107 gram substance gave 0.2697 gram Hg.

	Calculated for $HgCl_2,3HgO$.	I.	Found. II.	III.
Cl	7.70	7.78	7.72	....
Hg	87.08	....	....	86.80

As thus prepared, the substance forms distinct prisms. It is not changed by (*a*) light, (*b*) heating dry to 110°, or (*c*) boiling with a 7 per cent mercuric chloride solution. With excess of moist mercuric chloride it changes to $2HgCl_2,HgO$ without passing through any intermediate compound, such as

$HgCl_2,2HgO$. Heated with water, yellow tablets of penta-mercurtetroxychloride, $HgCl_2,4HgO$, are formed. These observations are contrary to those of Thümmel, who found that the substance, when heated dry, blackens below 180°, is unstable in the light, heated with water gives black $HgCl_2,2HgO$ and brown $HgCl_2,4HgO$, and with mercuric chloride solution gives black $HgCl_2,2HgO$. However, I found that impure samples behaved according to Thümmel's observations.

The density of this modification of tetramercurtrioxychloride was found to be 7.93. Besides this modification of tetramercurtrioxychloride, there are two others: One, brick-red, amorphous, was prepared according to Voit's[1] directions; the other, yellow plates, was prepared according to Millon.[2] I noted nothing particular about either. Since they could not be isolated without decomposition, their densities were not determined.

Pentamercurtetroxychloride, $HgCl_2.4HgO$.—(*a*) Yellow hexagonal plates. (*b*) Brown amorphous.

Both of these modifications are easily obtained pure by following Thümmel's[3] directions. I found the density of (*a*) to be 9.008, and of (*b*) to be 9.050.

Investigation of the Fusion of Mercuric Chloride with Mercuric Oxide.

Mercuric chloride and mercuric oxide, in various proportions, were carefully ground together, put into sealed tubes, and heated to 300° for six to eight hours. The resulting masses were ground, examined microscopically, and then treated with ether, first in a Soxhlet extraction apparatus and then by washing by decantation until the wash ether left no residue upon evaporation. Then the substances were examined again microscopically, and if apparently homogeneous, they were analyzed for chlorine and mercury. The same compound,—clear wine-red crystals of $HgCl_2,2HgO$,—was obtained in each of the following :

[1] Ann. Chem. (Liebig), **104**, 351.
[2] Ann. chim. phys., (3), **18**, 333.
[3] *Loc. cit.*

I. $10HgCl_2 + HgO$, red, heated six hours.
II. $2HgCl_2 + HgO$, red, heated six hours.
III. $HgCl_2 + HgO$, red, heated six hours.
IV. $HgCl_2 + 2HgO$, red, heated six hours.
V. $HgCl_2 + HgO$, red, heated three hours.
VI. $HgCl + HgO$, with a few drops of water, heated six hours.
VII. $10HgCl_2 + HgO$, yellow, heated six hours.
VIII. $HgCl_2 + HgO$, yellow, heated six hours.

Calculated for $HgCl_2,2HgO$.	Found.							
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Cl 10.07	10.3	9.90	9.99	10.05	9.90	10.14	10.08	9.97
Hg 85.38	85.38	....	85.08	....	85.16	....	....	....

Hence an excess of mercuric chloride over that required for the product $HgCl_2,2HgO$ always remained uncombined.

On the other hand, mixtures containing more oxide than is required for $HgCl_2,HgO$ resulted in the following :

(*a*) $HgCl_2 + 4HgO$, a dark-brown mass of pentamercurtetroxychloride not well crystallized.

(*b*) $HgCl_2 + 3HgO$, wine-red crystals of trimercurdioxychloride, mixed with brownish-yellow crystals, which were found to be pentamercurtetroxychloride.

(*c*) $HgCl_2 + 6HgO$, mixture of pentamercurtetroxychloride crystals with free oxide.

There are no methods known by which such mixtures as these may be separated, hence the microscope was the only means of examining them. The oxychloride $HgCl_2,4HgO$ was obtained pure for recognition and analysis by heating a mixture of $HgO + 2HgCl_2$ in a tube and keeping the empty end cooler than the other. Mercuric chloride distilled to this end, and in the other remained a homogeneous mass of black, shining crystals—hexagonal plates of a pale slate-blue (reddish-brown or yellow, according to thickness) color, which gave upon analysis :

I. 0.9804 gram substance gave 0.2557 gram AgCl.
II. 1.0326 grams substance gave 0.2693 gram AgCl.
III. 0.4226 gram substance gave 0.3722 gram Hg.

	Calculated for $HgCl_2,4HgO$.	I.	Found. II.
Cl	6.24	6.45	6.32
Hg	88.13	88.07	. . . .

Hence, an excess of mercuric oxide over that required for the product $HgCl_2,4HgO$ remained uncombined.

In these preparations only two distinct oxychlorides were formed :

$$HgCl_2,2HgO \qquad \text{and} \qquad HgCl_2,4HgO.$$
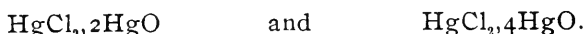
The other compounds André gives were probably mixtures.

The density of this form of trimercurdioxychloride is found to be 8.43 and of the pentamercurtetroxychloride 9.107.

The foregoing paper was finished several months ago, but I was delayed in sending it off for publication. In the meanwhile an article by Schlick[1] has appeared which I wish to note briefly.

The author's results, valuable as they are, do not support his conclusion as to the identity of the oxides when the facts presented in this paper are considered. In the first place, the only criterion Schlick used for distinguishing between the oxides was the color, which I have found to be unreliable; in the second place, it was to be expected, or at least quite likely that under the circumstances the solubilities of both forms appear to be the same because the form unstable at the temperature of the experiment is converted to the stable form.

In conclusion, I wish to thank Professor Felix Lengfeld for the kind assistance and valuable suggestions he has given me in the prosecution of this work.

I also wish to thank Miss H. Whitten and Mr. R. D. George for the favors shown me in the microscopical examinations of samples of the mercuric oxides.

[1] Ztschr. phys. Chem., **42,** 155.

THE DETERMINATION OF MOLECULAR WEIGHTS.

By H. C. Biddle.

The influence of a dissolved substance upon the vapor-pressure of its solvent was a subject of study as early as the time of Gay-Lussac. The first generalization of much importance, however, was made by Wüllner[1] in 1858. This investigator showed that in aqueous solutions of non-volatile substances, the lowering of the vapor-pressure was roughly proportional to the quantity of substance dissolved. In the investigations of Wüllner and of those immediately following him, attention was directed largely to the study of salt solutions,[2] consequently more than a quarter of a century elapsed before a clear insight into the phenomena of vapor-tension was gained. The extension of the study of vapor-pressures to solutions other than aqueous, we owe chiefly to Raoult.[3] This investigator had noted the close relation existing between the diminution of the vapor-pressure of a solution, the lowering of its freezing-point, and the number of molecules of the dissolved substance, and was led by these considerations to study the vapor-pressures of ethereal solutions. His work gave definition to the entire subject, and is undoubtedly the most important that has ever been done on the vapor-tension of solutions.[4]

Among his results the following are of particular consequence : The relative vapor-pressure, $\dfrac{f'}{f}$, between $0°$ and $22°$ is independent of the temperature ; the relative lowering of the vapor-pressure, $\dfrac{f-f'}{f}$, is proportional to the molecular concentration ; the depression, $f-f'$, produced in a solution of a non-volatile substance, is independent of the nature of that substance ; and the lowerings of vapor-pressure in various

---

[1] Pogg. Ann., **103**, 529 (1858) ; **105**, 85 (1858) ; **110**, 564 (1860).

[2] Panchon : Compt. rend., **89**, 752 (1879) ; Tammann : Wied. Ann., **24**, 523 (1885) ; Emden ; *Ibid*, **31**, 145 (1887); etc.

[3] Compt. rend., **103**, 1125 (1886).

[4] *Ibid.*, **104**, 976, 1430 (1887) ; **107**, 442 (1888). Ztschr. phys. Chem., **2**, 353 (1888). Ann. chim. phys., [6], **15**, 375 (1888).

solvents are the same when in their solutions the ratio of the number of molecules of solute to that of the solvent is the same.

Raoult indicated the possibility of employing the lowering of the vapor-pressure of a solution in determining the molecular weight of a dissolved substance. In his opinion, however, the experimental difficulties were such as to give preference to the cryoscopic and ebullioscopic methods.[1] Both Tammann[2] and Raoult[3] have called attention to the possible errors in measuring vapor-pressure which arise from the presence of dissolved gases and from variations in surface concentration due to unequal evaporation or condensation.

Numerous attempts have been made to devise a ready and accurate method for measuring the vapor-pressure of a solution.[4] Raoult[5] and the most of the experimenters before him employed the barometric vacuum over mercury. Beckmann[6] undertook the study of such measurements with the avowed purpose of designing an apparatus which could be used practically in determining the molecular weight from the lowering of the vapor-pressure.

He had recourse to the static method and employed first of all a modification of the barometric vacuum. The difficulties encountered, however, led him to abandon this. A partially static method gave somewhat better results, but it likewise proved inferior to the ebullioscopic method, to which he thereafter directed his attention.[7]

Dynamical methods of measuring the vapor-tension have also been worked out with varying degrees of success. The essential feature of one of these, first suggested by Ostwald, consists in determining the relative lowering of the vapor-pressure from the ratio of loss of weight of solvent to gain in weight of an absorption bulb, when a slow current of air is

[1] Ztschr. phys. Chem., **2**, 372, 373.

[2] Wied. Ann., **32**, 683 (1887).

[3] Ztschr. phys. Chem., **2**, 359.

[4] Moser : Wied. Ann., **14**, 72 (1881) ; Bremer : Rec. trav. chim. Pays-Bas., **6**, 122 (1887); and others.

[5] Ztschr. phys. Chem., *loc. cit.* ; Jour. de Phys., [2], **8**, 1 (1889).

[6] Ztschr. phys. Chem., **4**, 532 (1889).

[7] *Loc. cit.*

passed, in order, through solution, solvent, and absorption bulb.[1]

Kahlbaum[2] compares the static and dynamic methods and shows that both should yield like results.

Differential manometers of various forms for the direct measurement of differences in vapor-pressure have been suggested by Loeb,[3] Lord Kelvin,[4] Bleier and Kohn,[5] and others.

The following brief investigation was undertaken with the view of securing a serviceable apparatus for measuring, according to the static method, the difference in vapor-pressure between solution and solvent, and at the same time of simplifying the calculation of the molecular weight without introducing errors sufficiently large to vitiate the results.

As has been shown by Raoult, the lowering of the vapor-pressure of a solvent due to the presence of a non-volatile solute may be expressed by the well-known equation,

$$\frac{f-f'}{f} = \frac{n}{n+\mathrm{N}}.$$

When the concentration is low (not exceeding 7 molecules of solute to 100 molecules of solvent) there is equally applicable, as shown by the same investigator,[6] the expression

$$\frac{f-f'}{f} = \frac{n}{\mathrm{N}}.$$

Indeed this was the form first employed by Raoult in studying variations in vapor-tension.

In using the following apparatus there is no need that the molecular concentration should exceed that named. In these and similar determinations it is, consequently, much simpler to employ Raoult's second formula, $\frac{f-f'}{f} = \frac{n}{\mathrm{N}}$. We may regard as the "molecular depression" the diminution in vapor-tension of 100 grams of the solvent, produced by 1 gram

[1] Walker: Ztschr. phys. Chem., **2**, 602 (1888) ; Will and Bredig : Ber. d. chem. Ges., **22**, 1084 (1889) ; Orndorff and Carrell ; J. phys. Chem., **1**, 753 (1897).

[2] Ztschr. phys. Chem., **6**, 594 (1890) ; **13**, 14 (1894).

[3] *Ibid.*, **2**, 606.

[4] Nature, **55**, 273, 295 (1897).

[5] Monatsh. Chem., **20**, 505, 909 (1899).

[6] Compt. rend., **104**, 976.

molecular weight of substance dissolved in it. If we represent this constant by K and the number of grams of substance and of solvent by P and W, respectively, we readily obtain for a given solvent at a given temperature the equation,

$$M = K\frac{100}{f-f'}\cdot\frac{P}{W}.$$

This expression, which, as we see, is identical with that for the boiling-point apparatus of Beckmann, renders it unnecessary to ascertain the direct vapor-pressure of either solution, or solvent.

The apparatus used is adapted to measure directly the lowering of the vapor-pressure, $f-f'$. A differential manometer with an inner diameter of 4 mm. is provided with two glass stop-cocks, a and b. The flasks, C and C', into which, respectively, solution and solvent are introduced, are of nearly the same capacity (about 250 cc. each). The capillary tubes $L L'$ connecting the flasks with the manometer are of equal length and form one piece with the ground-glass stoppers $D D'$.

The attachment between capillary tubes and manometer is made with heavy-walled rubber tubing. Tubes $E E'$, with glass stop-cocks at $F F'$, pass through the stoppers to within 1 to 2 cm. of the bottom of the flasks. The upper portions of these tubes are graduated to 0.1 cc. and should have a capacity of 10 to 15 cc. To insure against leakage, the ground-glass connections $D D'$ are further sealed with mercury. A T at point H permits a ready exhaustion of the apparatus.

In conducting a determination, the flasks are held at a fixed temperature by immersion in a suitable thermostat. Stop-cock a is then opened, b closed, and the apparatus partially exhausted. Equilibrium is determined by the constancy of the manometric fluid when b is opened and a closed. Both stop-cocks of the manometer are now closed and into each flask, respectively, is introduced an equal volume of solution and solvent. After a few minutes b is opened and the reading taken when the height of the manometric fluid has become constant. Olive oil was used in the manometer, and this was
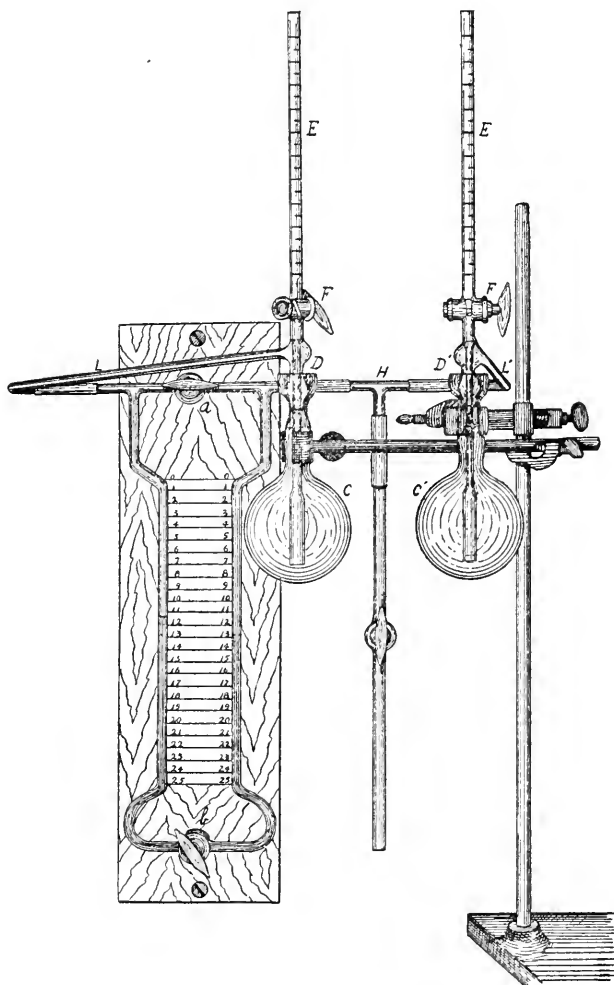
chosen chiefly because of its low vapor-tension. With a re-
duction of the internal pressure to about 300 mm. of mercury,
equilibrium is usually attained in fifteen to twenty minutes.

In measuring vapor-pressures the increased concentration
of the solution due to the partial evaporation of the solvent,
will lead, as Raoult[1] has indicated, to erroneous results, if no

[1] Ztschr. phys. Chem., *loc. cit.*

correction be made for this error. In the above apparatus this source of error is rendered negligible in the calculation by the introduction of a sufficient quantity of the solution (10 to 15 cc.).

As already noted, inaccuracies arise in such determinations from surface concentration.[1] This difficulty is obviated in the present case by the large surface of the liquid and by slightly agitating the flask. There was further indicated the necessity of eliminating from solution and solvent, when measuring their vapor-pressure, all foreign volatile substances such as gases. As may be readily seen, this source of error is negligible in the apparatus considered, provided only that the gaseous content of solution and solvent is the same. With this end in view, both liquids are introduced under as nearly as possible the same conditions of temperature and pressure. The slight difference in air-solubility naturally subsisting between solution and solvent is here ignored.

In the change of position of the manometric liquid, the equilibrium of the air-content of the two flasks is slightly disturbed. This will invariably render the observed difference in vapor-pressure less than that actually existing. The error here introduced, however, is proportional to the observed difference and consequently disappears in the constant K when this latter is experimentally determined.

The slight contamination of the liquids introduced by vaseline or similar lubricant on the stop-cocks $F F'$, might be considered as a source of error, but the results obtained indicate that this may be disregarded.

The solvent used in any case should not have a vapor-pressure much less than 225 mm. of mercury. Consequently, in employing liquids of lower vapor-pressure, it is better to work at a correspondingly higher temperature.

It was found that invariably the most satisfactory results were obtained by taking the mean of two determinations, the solution and the solvent in the two cases being interchanged between the two flasks. Each of the following readings represents the mean of two such determinations.

[1] Tammann and Raoult: *Loc. cit.*

The ether and carbon bisulphide used were carefully purified, the former being distilled over sodium.

Temperature variations in the thermostat were held within $0°.15$ C.

The pressure was reduced to 295–305 mm. and into each flask were introduced 10 cc. of liquid.

TABLE I.

Solvent, ether; $K = 260.00$; Temperature, $15°$.

Naphthalene.

$\dfrac{P}{W}$.	$f - f'$ in cm.	Molecular weight found	Molecular weight calculated.
0.0639	13.3	124.9	128
"	13.0	127.8	"
0.06565	13.3	128.4	"
"	13.33	128.0	"
0.0689	13.85	132.3	"
"	13.94	128.5	"
"	14.0	128.0	"

Cinnamic Acid.

0.05922	10.25	150.2	148
0.06716	11.65	149.9	"
"	12.0	145.5	"

Salicylic Acid.

0.06549	12.4	137.3	138
"	13.0	131.0	"
"	12.6	135.1	"

Iodine.

0.07139	7.4	250.8	254
"	7.5	247.5	"
"	7.3	254.2	"
"	7.4	250.8	"

Solvent, carbon bisulphide; $K = 171.50$: Temperature, $15°$.

Naphthalene.

0.0851	11.0	132.7	128
"	11.2	130.3	"
0.07348	9.9	127.3	"
"	9.7	129.9	"

Phenanthrene.

$\dfrac{P}{W}$	$f-f'$ in cm.	Molecular weight found.	Molecular weight calculated.
0.06025	6.05	170.8	178
0.06971	7.05	169.6	"
"	7.00	170.8	"

Sulphur.

0.07435	4.9	260.2	256
"	"	"	"

Phosphorus.

0.07881	10.45	129.3	124
"	10.3	131.2	"

Iodine.

0.08115	5.5	253.0	254
"	5.8	240.0	"
"	5.4	257.8	"

The molecular weight of iodine as above determined is of some interest in view of the speculation that has obtained regarding the molecular aggregation of the element in different solvents. As is well known, iodine dissolves in some liquids as carbon bisulphide and the hydrocarbons with a violet color, in still others as alcohol, ether, and other alcoholic derivatives with a brownish-yellow color. Other solvents again yield intermediate gradations of color. It was early inferred that the color differences were due to a difference in molecular aggregation, and some of the experimental data seemed to favor this conclusion. Wiedemann[1] called attention to the fact that the solution in carbon bisulphide, when cooled with carbon dioxide and ether, became brownish-red. This result, doubted by Arctowsky,[2] was later confirmed by Krüss and Thiele.[3] On the other hand, brown solutions in the esters of the fatty acids become violet on warming to 80° C. Gautier and Charpy[4] for a time thought that they had discovered a difference in chemical behavior between violet and brown solutions.

[1] Wied. Ann., **269**, 580 (1888).

[2] Ztschr. anorg. Chem., 6, 403 (1894).

[3] *Ibid.*, **7**, 70 (1894).

[4] Compt. rend., **111**, 645 (1890) ; Compare Beckmann and Stock : Ztschr. phys. Chem., **17**, 130 (1895).

The difference in the absorption spectra of variously colored solutions was also advanced as indicating a difference in molecular complexity.[1]

An attempt was made by Loeb,[2] working under Ostwald, to determine the molecular condition of iodine in solution from the change in vapor-pressure of the volatile solvent. His results led him to believe that in ether the molecule is I_4, while in carbon bisulphide it lies between I_2 and I_3. His method, however, was difficult to carry out, and ignored several of the sources of error already considered.

The careful work of Beckmann,[3] Nernst,[4] Krüss and Thiele,[5] and others,[6] has, however, shown conclusively that the molecule of iodine in the different solvents studied is diatomic, irrespective of the color of the solution.

Alcohol, as a solvent, does not readily lend itself to the determination of the molecular weight of iodine. Of the two methods commonly employed in such determinations, one is inapplicable because of the low freezing-point of the solvent, and the other appears to be somewhat unreliable because of the action of the element on boiling alcohol.[7] At the same time it may be noted that fairly concordant results have been obtained by the latter method.[8] The vapor-tension of alcohol at 15° to 20° is insufficient to afford trustworthy data by employing at those temperatures the apparatus described in this paper.

In connection with the results as tabulated above, an attempt was made to measure the osmotic pressure of a solution of iodine in alcohol.

The first exact quantitative measurements of osmotic pressure we owe to the painstaking work of Pfeffer.[9] He employed aqueous solutions and showed very clearly in such

[1] Compt. rend., **110**, 189 ; Rigollot: *Ibid.*, **112**, 38 (1891).

[2] Ztschr. phys. Chem., **2**, 606.

[3] *Ibid.*, **5**, 76 (1889) ; **17**, 107 (1895).

[4] *Ibid.*, **6**, 16 (1890).

[5] Ztschr. anorg. Chem., **7**, 52 (1894).

[6] Hertz : Ztschr. phys. Chem., **6**, 358 (1890).

[7] Krüss and Thiele : Ztschr. anorg. Chem., **7**, 61.

[8] Beckmann and Stock : Ztschr. phys. Chem., **17**, 117.

[9] Osmotische Untersuchungen, Leipzig, 1877.

cases the close relation between the osmotic pressure and the molecular concentration of the dissolved substance.

Since Pfeffer's work but little advance has been made in the methods of measuring osmotic pressure, although recently Morse and Frazer[1] have prepared a cell which seems to be particularly well adapted for recording high pressures. Aside from indirect determinations, however, such as those which may be derived from the boiling- or freezing-point methods or from the method suggested by Noyes and Abbott,[2] apparently no attempt has yet been made to measure directly the osmotic pressure of solutions other than aqueous.

In the following measurements a slight modification of Pfeffer's apparatus was used. It was found to be a comparatively simple matter to obtain serviceable cells in aqueous solutions, but the successful employment of these cells in alcoholic solutions proved somewhat difficult. The results obtained, however, point conclusively to the diatomic condition of iodine in the solvent and confirm the ebullioscopic determinations of Beckmann and Stock.[3]

A porous clay cell of about 25 cc. capacity was treated successively with dilute potassium hydroxide and hydrochloric acid (about 3 per cent), and was finally well washed with distilled water. Into the neck of the cell was then sealed securely with Portland cement a glass ⊤. As soon as the cement had hardened, the cell was thoroughly injected with water and a membrane of copper ferrocyanide deposited according to the method employed by Pfeffer. A semi-permeable membrane was formed in this way, which would readily support a pressure of 1 atmosphere. The cell thus prepared was freed from soluble salts by prolonged treatment with distilled water. It was then transferred through water-alcohol of gradually increasing alcoholic strength to the ordinary 95 per cent alcohol.

An open manometer, with a capillary tube of 1.5 mm. inner diameter, was used to record the pressure. Variation in the

[1] This JOURNAL, **26**, 80 (1901) ; **28**, 1 (1902).
[2] Ztschr. phys. Chem., **23**, 56 (1897) ; also Goodwin and Burgess : Phys. Rev., **7**, 171 (1898).
[3] *Loc. cit.*

concentration of the solution due to interaction of the iodine and the mercury of the manometer extended only a few centimeters along the capillary above the surface of the mercury. The cell was closed and connected with the manometer by
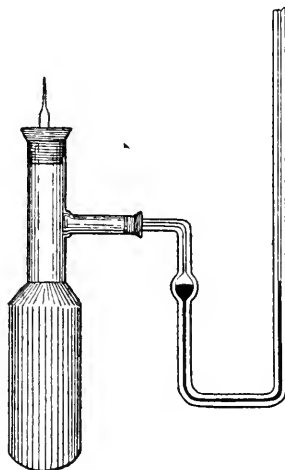
ordinary well-fitted corks, which were sealed externally to the glass ⊤ to preclude possibility of slipping.

The use of copper ferrocyanide as a membrane with iodine is not, as might be supposed, open to objection because of the oxidizing influence of the latter. While chlorine and bromine act upon this salt immediately, it is unaffected, at the ordinary temperature, after an hour's contact with an alcoholic solution of iodine such as was used in these determinations.[1]

The rise of the mercury in the manometer was much more rapid with alcoholic than it was with aqueous solutions of corresponding molecular concentration. The maximum pressure was attained in sixty to seventy-five minutes, and this pressure remained constant for nearly the same length of time. The molecular weight was calculated from the expression,

$$M = 22.4 \times 760 \times (1 + \alpha t)\frac{R}{P},$$

[1] That no change had occurred was shown by filtering and titrating the filtrate in the usual way with a solution of thiosulphate.

where M is the molecular weight, R the amount of substance dissolved in 1 liter of the solution, and P the osmotic pressure expressed in mm. of mercury.

TABLE II.

R.	Temperature.	P.	Molecular weight found.	Molecular weight calculated.
3.98	12°	265.1	266.8	254
4.14	17°	260.3	287.6	"
4.14	17°	277.8	269.5	"

In the above measurements of osmotic pressure I have been assisted by Miss Myra Winn, and in those of vapor-pressure by Mr. M. L. Chappell, and I take this occasion to express my appreciation of their earnest and careful work.

CHEMICAL LABORATORY, UNIV. OF
CALIFORNIA, BERKELEY, CAL.,
December 20, 1902.

DIPHENYLSTYRYLCARBINOL.

BY ELMER P. KOHLER.

Results recently obtained by a number of investigators show that there is a remarkable difference between the properties of those tertiary alcohols which contain at least one alkyl group and those which contain only aryl groups. Substances like diphenylmethylcarbinol behave essentially like tertiary alcohols that contain only alkyl groups,[1] while triphenylcarbinol and its substitution-products are far more reactive than any aliphatic alcohols. They are easily reduced to the corresponding hydrocarbons,[2] they react, in the cold, with hydroxylamine and acid sulphites,[3] they can be condensed with substances like aniline and phenol,[4] and they combine with strong acids to form colored salts.[5] In view of these differences it was important to prepare and study tertiary alcohols which, like diphenylstyrylcarbinol,

$$(C_6H_5)_2(C_6H_5CH : CH)COH,$$
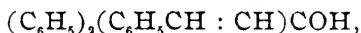
[1] Klages : Ber. d. chem. Ges., **35,** 2646.
[2] Herzig and Wengraf : Monatsh., **22,** 604.
[3] Baeyer and Villiger : Ber. d. chem. Ges., **35,** 3016.
[4] Baeyer and Villiger : *Ibid.,* **35,** 3018.
[5] Kehrmann : *Ibid.,* **34,** 3815.

and the corresponding substance with two double linkages,

$$(C_6H_5)_2(C_6H_5CH : CHCH : CH)COH,$$
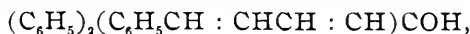
contain at least one alkylene group.

This paper contains the results obtained by a study of the former of these substances.

I. Preparation and Properties of Diphenylstyrylcarbinol.

Diphenylstyrylcarbinol can be made by the general reactions that Grignard[1] employed for making tertiary alcohols. In the beginning considerable difficulty was experienced because of the difference in the way in which saturated and unsaturated compounds react with organic magnesium compounds. The reactions that were expected to give a magnesium derivative of the alcohol are represented by the following equations :

I. $C_6H_5CH : CHCOC_6H_5 + C_6H_5MgBr =$

$$C_6H_5CH : CHC{\overset{\textstyle /C_6H_5}{\underset{\textstyle \backslash C_6H_5}{—OMgBr}}} ;$$

II. $C_6H_5CH : CHCO.OC_2H_5 + 2C_6H_5MgBr =$

$$C_6H_5CH : CHC{\overset{\textstyle /C_6H_5}{\underset{\textstyle \backslash C_6H_5}{—OMgBr}}} + Mg{\overset{\textstyle /OC_2H_5}{\underset{\textstyle \backslash Br}{}}} ;$$

III. $C_6H_5CH : CHCOCl + 2C_6H_5MgBr =$

$$C_6H_5CH : CHC{\overset{\textstyle /C_6H_5}{\underset{\textstyle \backslash C_6H_5}{—OMgBr}}} + Mg{\overset{\textstyle /Cl}{\underset{\textstyle \backslash Br}{}}} .$$
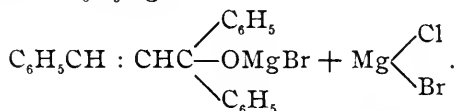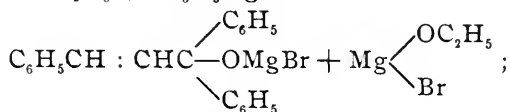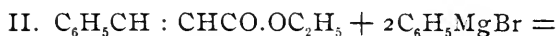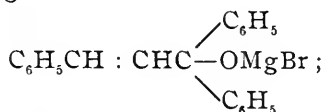
None of these reactions, however, gave the desired substance when the quantities used were those calculated from the above equations—each gave a substance of much greater molecular weight.

The magnesium compound obtained by the first reaction, for example, when decomposed with ice-water, gave a substance whose composition and molecular weight are represented by the formula $C_{36}H_{30}O_2$. Since this corresponds to the

---

[1] Compt. rend., **132**, 1182.

composition of a substance formed by the condensation of 1 molecule of diphenylstyrylcarbinol, $C_{21}H_{18}O$, and 1 molecule of benzylideneacetophenone, $C_{15}H_{12}O$, it seemed evident that the magnesium compound first formed in accordance with reaction I. subsequently combines with a molecule of the unchanged ketone. The concentration, the temperature, and the general method of procedure were changed in a variety of different ways without any material effect on the final result. It was observed, however, that the reacting liquid turned to a pale-yellow color when approximately one-half of the calculated amount of ketone had been added, and a very fair yield of the desired alcohol was obtained when the liquid was poured into ice-water immediately after the appearance of the yellow color.

To get the unsaturated alcohol, therefore, it is necessary to use 2 molecules of the magnesium compound to one of the unsaturated ketone. The best results were obtained when the ethereal solution of the ketone was added, drop by drop, at the top of an inverted condenser, which was connected with a flask in which the magnesium compound was kept boiling rapidly. As soon as all the ketone had been added the magnesium compound was poured into cold dilute sulphuric acid, the ethereal solution distilled in a water-bath, and the residue purified by recrystallization from alcohol.

Fifty-four grams of benzylideneacetophenone added to a solution obtained by dissolving 12 grams of magnesium in 80 grams of brombenzene and 750 grams of ether, gave 64 grams of diphenylstyrylcarbinol—about 90 per cent of the calculated amount.

The analyses gave the following results :

I. 0.1554 gram substance gave 0.5036 gram CO_2 and 0.0895 gram H_2O.

II. 0.1912 gram substance gave 0.6181 gram CO_2 and 0.1121 gram H_2O.

	Calculated for $C_{21}H_{18}O$.	Found. I.	II.
C	88.12	88.36	88.16
H	6.30	6.39	6.51

The molecular weight was determined in boiling acetone.

Table I.

K = 17.10.

Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
7500	0.6190	0.055	256
"	1.2100	0.108	276
"	1.7350	0.158	273
		Calculated for $C_{21}H_{18}O$,	286

Diphenylstyrylcarbinol crystallizes well in colorless needles, which melt at 96°. It is very soluble in acetone, chloroform, benzene, and boiling alcohol; moderately soluble in cold alcohol and ether; very sparingly soluble in low-boiling ligroin. Under diminished pressure it distils without decomposition. When slowly heated under atmospheric pressure, most of it distils unchanged. The remainder undergoes far-reaching decomposition, the distillate containing stilbene and benzophenone while the residue is a gum from which no pure substances could be obtained.

Halochromism.—The alcohol dissolves in concentrated sulphuric acid and forms a lemon-yellow solution from which water reprecipitates the original substance. Since the only alcohols which are known to exhibit this property of " halochromism" are triphenylcarbinol and its substitution-products, it was important to prove beyond the possibility of mistake that the change in color is not due to a trace of some impurity like an unsaturated ketone. The alcohol was therefore repeatedly recrystallized from each of the different solvents above referred to. Since this did not change the result, it was transformed into the chloride with phosphorus pentachloride; the chloride, which crystallizes better even than the alcohol, was carefully purified by recrystallization from glacial acetic acid and then changed back into the alcohol with zinc dust and acetic acid. The resulting alcohol gave the same shade and intensity of color as the original product.

Towards strong acids, therefore, diphenylstyryl alcohol behaves differently from tertiary alcohols which contain an alkyl group. Its halochromism is very weak. A comparison

with triphenylcarbinol, made by the method of Baeyer and Villiger,[1] showed that the halochromism of the latter is about three hundred times as strong as that of the diphenylstyryl-carbinol.

Reduction.—The alcohol is reduced only with the greatest difficultly and no reducing agent that attacked the hydroxyl group was found. Sodium and sodium amalgam, acting on the alcoholic solution of the substance, slowly reduce it, giving an oil. This does not combine with bromine, but forms an alcoholate with metallic sodium. It is probably the saturated alcohol.

Zinc and glacial acetic acid give a well defined solid. Ten grams of zinc dust were added to 5 grams of the alcohol dissolved in 50 grams of glacial acetic acid. After boiling the mixture for five hours, compact, lustrous prisms began to separate on the walls of the flask. After boiling for twenty hours the acid was poured into water and the solid that separated purified by crystallization from alcohol. The product is moderately soluble in chloroform and benzene ; slightly soluble in glacial acetic acid, alcohol, and acetone ; insoluble in ligroin. It crystallizes in small plates that melt at 195°.

The analyses gave the following results :

I. 0.1497 gram substance gave 0.4085 gram CO_2 and 0.0917 gram H_2O.

II. 0.1991 gram substance gave 0.6393 gram CO_2 and 0.1202 gram H_2O.

	Calculated for $C_{21}H_{19}O$.	Found.	
		I.	II.
C	87.8	87.5	87.6
H	6.6	6.8	6.7

The molecular weight was determined in boiling acetone.

Table II.

$$K = 17.10.$$

Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
77.7010	0.2123	0.080	584
''	0.5338	0.200	589
	Calculated for $(C_{21}H_{19}O)_2$,		574

[1] Ber. d. chem. Ges., **35**, 3020.

The substance is evidently a dimolecular reduction-product formed according to the equation :

$$2C_6H_5CH : CHC\begin{smallmatrix} C_6H_5 \\ | \\ \end{smallmatrix}-OH \ + 2H \quad = \quad C_6H_5CHCH_2C\begin{smallmatrix} C_6H_5 \\ \\ C_6H_5 \end{smallmatrix}-OH$$

$$C_6H_5CHCH_2C\begin{smallmatrix} C_6H_5 \\ \\ C_6H_5 \end{smallmatrix}-OH$$

or

$$C_6H_5CH_2CHC\begin{smallmatrix} C_6H_5 \\ \\ C_6H_5 \end{smallmatrix}-OH$$

$$C_6H_5CH_2CHC\begin{smallmatrix} C_6H_5 \\ \\ C_6H_5 \end{smallmatrix}-OH$$
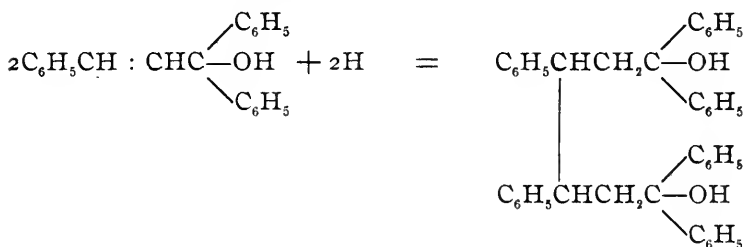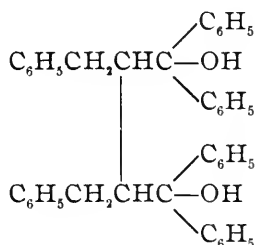
Oxidation.—Although diphenylstyrylcarbinol contains a double linkage it is not easily oxidized. Neither acid nor alkaline solutions of potassium permanganate attack it in the cold, and even boiling solutions of permanganate are reduced by it very slowly. Five grams of the alcohol were suspended in 750 cc. of a 5 per cent solution of sodium hydroxide. Potassium permanganate was added to the boiling liquid, in small quantities, until the color of the permanganate no longer disappeared. The liquid was then distilled in a current of steam which carried over an oil that solidified on standing. The resulting solid melted at 46° and gave a phenylhydrazone melting at 137°. It was pure benzophenone. The residue left after the distillation with steam was acidified, treated with hydrogen sodium sulphite to dissolve the oxides of manganese, and again distilled in a current of steam. The distillate contained only benzoic acid. The liquid left in the flask after the second distillation was extracted with ether, but no organic substance was found in it. The products of the oxidation were, therefore, benzoic acid and benzophenone.

The oxidation can be represented by the following equations :

$$\text{I. } C_6H_5CH : CHC{\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{—OH}}} + 4O =$$

$$C_6H_5COOH + (C_6H_5)_2C{\overset{OH}{\underset{COOH}{\diagup\diagdown}}} ;$$

$$\text{II. } (C_6H_5)_2C{\overset{OH}{\underset{COOH}{\diagup\diagdown}}} + O = (C_6H_5)_2CO + H_2O + CO_2.$$
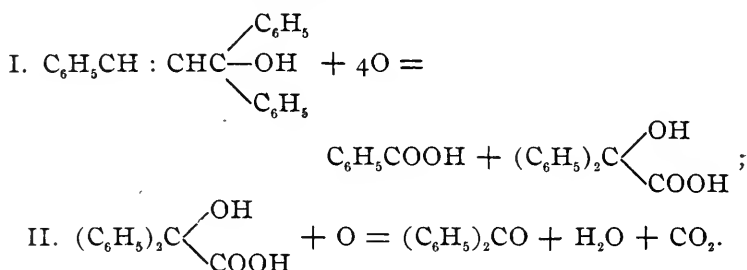
A solution of chromic acid in glacial acetic acid slowly oxidizes the alcohol in the cold. Carbon dioxide is given off and the other products of oxidation are the same as those obtained with the boiling solution of alkaline permanganate.

Addition of Bromine.—The alcohol, dissolved in chloroform or carbon disulphide, slowly combines with bromine in the cold. The resulting addition-product is so unstable that it loses hydrobromic acid even when the solvent is evaporated in a vacuum. The only substance that was obtained in pure condition was a monobrom substitution-product. This is easily made by adding the calculated amount of bromine to a solution of the alcohol in chloroform, warming the mixture until the color of the bromine disappears, and pouring the product into boiling alcohol. On cooling the solution, pure bromdiphenylstyrylcarbinol crystallizes out in colorless plates that melt at 163°.

0.2740 gram substance gave 0.6922 gram CO_2 and 0.1158 gram H_2O.

	Calculated for $C_{21}H_{17}OBr$.	Found.
C	69.04	69.91
H	4.63	4.72

The substance is readily soluble in chloroform and ether, slightly soluble in alcohol.

Diphenylstyrylchlormethane.—Tertiary alcohols that contain an alkyl group readily react with hydrochloric acid and form the corresponding chlorides.[1] Triphenylcarbinol and its de-

[1] Klages : Ber. d. chem. Ges., **35**, 2633.

rivatives react less readily with hydrochloric acid, but under suitable conditions these also are transformed into the corresponding chlorides.[1] Diphenylstyrylcarbinol does not seem to react with hydrochloric acid under any conditions. The dry gas was passed into the fused alcohol, into cold and boiling ethereal solutions of the alcohol, and into its solution in glacial acetic acid. In each case the substance was recovered unchanged. With phosphorus pentachloride, however, the hydroxyl group can be replaced by chlorine.

A mixture of 25 grams of the alcohol and 20 grams of phosphorus pentachloride was warmed on a water-bath. The reaction commenced at the melting-point of the chloride. As soon as hydrochloric acid ceased to be given off, the flask was connected with a pump and heated in a water-bath until all the chlorides of phosphorus were removed. The residue remained liquid when cooled in a freezing-mixture, but solidified almost immediately after it was poured into low-boiling ligroin. The resulting solid was purified by repeated recrystallization from low-boiling ligroin.

The analyses gave the following results :

I. 0.1896 gram substance gave 0.5737 gram CO_2 and 0.0969 gram H_2O.

II. 0.2282 gram substance gave 0.6900 gram CO_2 and 0.1150 gram H_2O.

	Calculated for $C_{21}H_{17}Cl$.	I.	II.
C	82.73	82.61	82.50
H	5.58	5.63	5.58

The chloride crystallizes beautifully in large, lustrous, monoclinic prisms that melt at 91°. It is readily soluble in boiling alcohol and glacial acetic acid, moderately soluble in boiling ligroin and cold alcohol, almost insoluble in cold ligroin. The best crystals are obtained from glacial acetic acid.

Diphenylstyrylchlormethane is a remarkably inactive substance. After boiling it with a 10 per cent solution of sodium hydroxide for an hour, it was impossible to detect any chlorine in the solution. A boiling alcoholic solution of potassium hydroxide, however, slowly eliminates the chlorine and

[1] Baeyer and Villiger : *Ibid.*, **35**, 3031.

regenerates the alcohol. Zinc does not attack the substance when it is dissolved in indifferent solvents like benzene, alcohol, or ethyl acetate. In glacial acetic acid zinc dust slowly replaces the chlorine by hydroxyl. The process is greatly accelerated by the addition of a small quantity of copper acetate. The main product is always the carbinol. This is mixed with a small quantity of the dimolecular reduction-product previously described and a trace of an oil which appears to be an acetate, since it gives off acetic acid when distilled under diminished pressure.

II. Other Substances Obtained by the Reaction between Benzylideneacetophenone and Phenylmagnesium Bromide.

Under the preparation of diphenylstyrylcarbinol it was stated that when more than 0.5 molecule of benzylideneacetophenone is added to a solution of 1 molecule of phenylmagnesium bromide, the solution turns yellow. On further addition of ketone to this yellow solution a pasty mass separates from the solution. This increases in amount until 2 molecules of ketone have been added to 1 molecule of the bromide. When this paste is decomposed with water it gives a substance which, after recrystallization from acetone, melts at 180°.

An analysis of this substance gave the following results :

I. 0.2086 gram substance gave 0.6679 gram CO_2 and 0.1143 gram H_2O.

II. 0.1840 gram substance gave 0.5872 gram CO_2 and 0.1023 gram H_2O.

	Calculated for $C_{18}H_{15}O$.	I.	II.
C	87.44	87.32	87.01
H	6.07	6.08	6.17

The molecular weight was determined in boiling acetone.

Table III.

$K = 17.10.$

Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
76.625	0.6023	0.027	498
``	1.1460	0.050	511
``	1.7970	0.080	500
	Calculated for $(C_{18}H_{15}O)_2$,		494

The substance is readily soluble in acetone, benzene, and boiling glacial acetic acid ; sparingly soluble in alcohol and ether ; insoluble in low-boiling ligroin. When distilled under a pressure of 20 mm. it decomposes into benzylidene-acetophenone, diphenylstyrylcarbinol, and a yellow oil of unknown composition. It dissolves in concentrated sulphuric acid, forming a blood-red solution.

The structure of this substance has not yet been established with certainty, but the method of formation, composition, and behavior on distillation leaves no doubt that it results from the combination of 1 molecule of benzylideneacetophenone with 1 molecule of diphenylstyrylcarbinol. Since it dissolves in sulphuric acid and gives a deep-red solution, the union of the two substances probably takes place at the double linkage of the unsaturated carbinol, leaving intact the double linkage of the ketone. This leads to the possible formulas :

$$C_6H_5CH.CH_2C{\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_5}{—OH}}}$$
$$C_6H_5CH : C.COC_6H_5$$
I.

$$C_6H_5CH_2CHC{\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_5}{—OH}}}$$
$$C_6H_5CH : C.COC_6H_5$$
II.
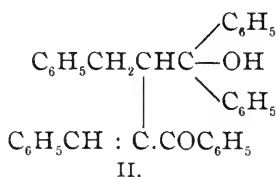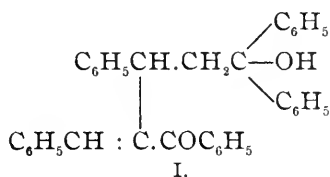
Each of these formulas explains the known properties of the substance. Formula I. is the more probable of the two since it represents a form of condensation that is known to take place with unsaturated acids[1] and unsaturated ketones.[2] In any case, since other unsaturated ketones give similar condensation-products, it will probably not be difficult to select materials in such a way that the structure of the product and, therefore, the general method of condensation can be determined by direct experiment.

The ethereal solution from which the magnesium derivative of the substance just described separates in the form of a paste, contains a third product of the reaction between benzylidene-acetophenone and phenylmagnesium bromide. This is a

[1] Michael: J. prakt. Chem., [2], **35**, 349; **37**, 522. Auwers : Ber. d. chem. Ges., **24**, 307.
[2] Knoevenagel: Ann. Chem. (Liebig), **281**, 24. Kostanecki : Ber. d. chem. Ges., **29**, 1488.

magnesium compound which is soluble in ether and which is formed in much larger amount when 1 molecule of the ketone is added to 1 molecule of the bromide. On decomposition with water it yields a viscous liquid, which it has not yet been possible to get in a perfectly pure condition. The crude product contains a small quantity of diphenylstyrylcarbinol, which can be removed by oxidation with chromic acid, and some of the condensation product which can be removed by extracting the ligroin solution with small quantities of concentrated sulphuric acid. The residue left after removing the ligroin is a clear, colorless oil, which decomposes on distillation under diminished pressure. The distillate contains large quantities of stilbene mixed with a small quantity of benzophenone. The oil imparts a faint yellow color to sulphuric acid. It may be a tertiary alcohol formed by the action of phenylmagnesium bromide on the condensation-product described above.

The reaction between benzylideneacetophenone and phenylmagnesium bromide seems to take place in the following stages :

1. Every drop of the solution of the ketone produces a faint-yellow precipitate, which immediately redissolves as long as the solution contains at least 2 molecules of the bromide for every molecule of ketone. This is probably represented by the following equations :

I. $C_6H_5CH : CHCOC_6H_5 + C_6H_5MgBr =$

$$C_6H_5CH : CHC\overset{\displaystyle /C_6H_5}{\underset{\displaystyle \backslash C_6H_5}{-}}OMgBr ;$$

(Yellow precipitate.)

II. $C_6H_5CH : CHC\overset{\displaystyle /C_6H_5}{\underset{\displaystyle \backslash C_6H_5}{-}}OMgBr + C_6H_5MgBr =$

$$\left(C_6H_5CH : CHC\overset{\displaystyle /C_6H_5}{\underset{\displaystyle \backslash C_6H_5}{-}}OMgBr \right)(C_6H_5MgBr).$$

(Soluble in ether).
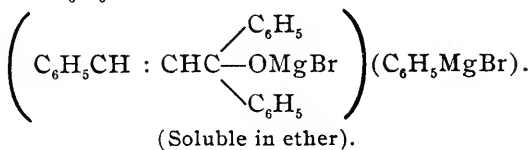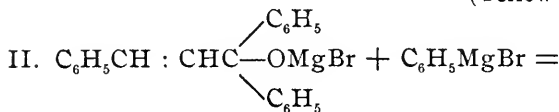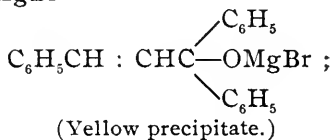
That such double compounds are capable of existing was shown by Grignard,[1] who found that allyl iodide forms the compound $C_3H_5I.C_3H_5MgI$, and that this compound does not give clean reactions.

If the mixture is decomposed with ice-water at this stage, the product is pure diphenylstyrylcarbinol.

2. The double compound reacts with more of the ketone:

$$\left(C_6H_5CH : CHC\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_5}{-OMgBr}} \right) (C_6H_5MgBr) +$$

$$3C_6H_5COCH : CHCOC_6H_5 =$$

$$2\left(\begin{array}{c} C_6H_5CH.CH_2C\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_5}{-OMgBr}} \\ | \\ C_6H_5CH : \overset{\cdot}{C}COC_6H_5 \end{array} \right).$$
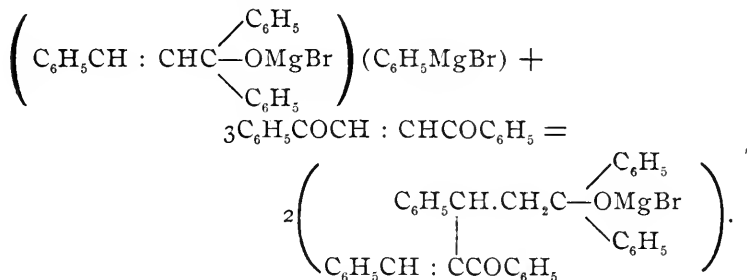
If the mixture is decomposed at this stage the product is the substance $C_{36}H_{30}O_2$.

III.
$$\begin{array}{c} C_6H_5CH.CH_2C\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_5}{-OMgBr}} \\ | \\ C_6H_5CH{:}CCOC_6H_5 \end{array} + C_6H_5MgBr =$$

$$\begin{array}{c} C_6H_5CH.CH_2C\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_5}{-OMgBr}} \\ | \\ | \\ C_6H_5CH : CC\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_5}{-OMgBr}} \end{array}$$
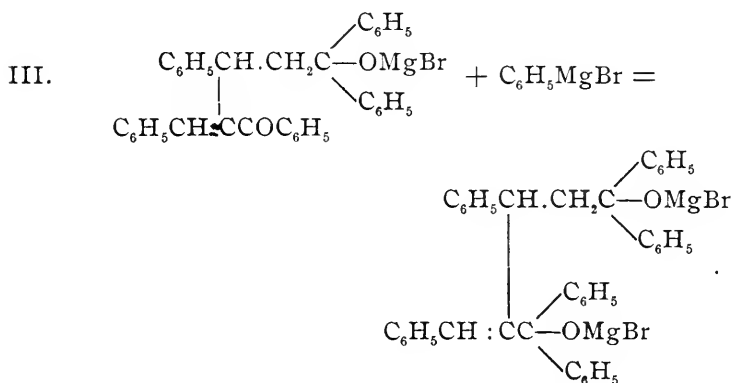
The oil described above is probably the product of decomposition at this stage.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE.

[1] Ann. chim. phys., [7], **24**, 433.

THE ACTION OF ZINC ON TRIPHENYLCHLOR-METHANE.

By M. Gomberg.

The recent paper by J. F. Norris and L. R. Culver,[1] under the above title, requires some corrections in regard to the references made by the authors to my papers.

Action of Sodium.

Norris and Culver[2] say : " It was shown in the same paper that, under certain conditions, triphenylchlormethane reacts with sodium, contrary to the observations of Gomberg." In turning to the first paper of Norris and Sanders, to which the reference is made, we find the following statement :[3] " The solution of the halogen compound (triphenylchlormethane) was allowed to stand two weeks in contact with sodium and, finally, was heated to boiling for an hour. As no change was apparent, the ethereal solution was decanted and evaporated to crystallization. The compound obtained was shown to be triphenylchlormethane." It was only on the addition of brombenzene to the above mixture that a reaction took place. In my short paper of two years ago the following explanation is given in regard to this reaction :[4] " Furthermore if the substance is really identical with the peroxide mentioned, it is not the result of the action of sodium upon a mixture of the two halogen compounds, but is formed by action of the atmospheric oxygen upon the unsaturated hydrocarbon (triphenylmethyl) which must have resulted in some way from the action of sodium upon triphenylchlormethane alone. Experiments show that small quantities of the triphenylmethyl are produced in this way."

Is the Reaction Quantitative?

Norris and Culver say :[5] " At the beginning of the work

[1] This Journal, **29**, 129 (1903).
[2] *Ibid.*, **29**, 130 (1903).
[3] *Ibid.*, **25**, 58 (1901).
[4] J. Am. Chem. Soc., **23**, 110 (1901).
[5] This Journal, **29**, 132 (1903).

it was found that the statement of Gomberg was incorrect, that when the reaction between zinc and triphenylchlormethane took place in benzene solution the metal reacts quantitatively according to the following equation :
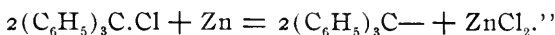
$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C- + ZnCl_2.''$$

In turning to the reference made by the authors to my paper in respect to this question, we see at once that there is no such statement either made or implied. We read :[1] '' The zinc removes the halogen from triphenylchlormethane quantitatively.'' And this statement is based not upon the results of a '' single,'' but of three experiments. That the whole of the chlorine is in the sirupy mass which separates in this reaction there was no doubt. But that the reaction, in so far as the production of triphenylmethyl is concerned, was not quantitative, I was well aware, and hence the statement on the very next page of the same paper :[2] '' Twenty grams of the halogen compound (triphenylchlormethane) give about 12 grams of the peroxide.'' The theoretical quantity is 18.6 grams. In another paper, which appeared a few months later,[3] we find the following statement : '' It was stated in my preliminary paper that only about two-thirds of the theoretical quantity of the unsaturated hydrocarbon is formed. The nature of the other products is being studied and I find that this varies according to the metal and solvent employed.'' Again, in a paper of still later date I say :[4] '' Strictly quantitative experiments on samples of 20 grams of triphenylchlormethane proved that the hydrocarbon can be obtained in yields of from 85 to 90 per cent of the calculated amount.'' I have spent a great deal of time and labor in order to determine how nearly quantitative the reaction is. Many data have been accumulated, but their publication is deferred to a later date, because I believe conditions will be found which will give still better results. Such ideal conditions, it is thought, have been found in the action of molecular silver. The reaction has been al-

[1] J. Am. Chem. Soc., **22**, 761 (1900).
[2] *Ibid.*, **22**, 762 (1900).
[3] *Ibid.*, **23**, 110 (1901).
[4] *Ibid.*, **24**, 628 (1902). Compare especially J. Am. Chem. Soc., **24**, 600.

lowed to proceed for several months, but the products have not as yet been further examined.

Formation of the Double Salt with Zinc Chloride.

Norris and Culver say :[1] "During the course of the reaction a thick, dark mass separates, which Gomberg assumed to be a compound of benzene and zinc chloride. Gomberg, in a later paper, briefly mentioned this mistake, but he has reported no further work to test this point." The authors also describe how they found out that this gummy mass is a compound of zinc chloride and triphenylchlormethane. No analysis of this compound was made by the authors.

The following is a quotation from my third paper,[2] where the action of zinc upon triphenylchlormethane in ether is described : " The viscous mass which is formed at the beginning of the reaction is not zinc chloride, but a double salt of it with triphenylchlormethane. Zinc chloride, I find, is soluble in ether, while the double salt is not. The thick yellow mass which was described under the experiments with benzene is also a double salt of a similar or of identical composition, and not a compound of zinc chloride with benzene, as has been previously supposed. Such a double salt, when treated with water, would give up all its chlorine to the latter, and this accounts for the somewhat misleading results which were obtained in the estimation of chlorine in the insoluble residue from benzene. The same double salt is formed with the greatest readiness when a solution of zinc chloride in ether or in acetic ether is added to a solution of triphenylchlormethane in benzene or in absolute ether. All attempts to bring it to crystallization have failed, but a number of other double salts of triphenylhalogenmethanes, and especially of tritolylchlormethane, were obtained in sufficient purity to establish the remarkable tendency of these halogen bodies towards the formation of double compounds with metallic salts."

A more detailed description of the composition and of the reactions of these interesting compounds is to be found in my fourth paper.[3] Quantitative results, showing that the reac-

[1] This JOURNAL, **29**, 132 (1903).

[2] J. Am. Chem. Soc., **23**, 4971 (1901).

[3] *Ibid.*, **24**, 601, 622 (1902).

tion in benzene proceeds probably according to the equation

$$3(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C + ZnCl_2.(C_6H_5)_3C.Cl,$$

are given in my sixth paper.[1]

Action of Zinc in Ethyl Acetate.

Norris and Culver then describe the action of zinc upon triphenylchlormethane in ethyl acetate. Their results confirm fully those given by myself: No hydrogen is given off; the unsaturated hydrocarbon is formed, which on exposure to air gives the peroxide. They also say :[2] "The filtrate from the peroxide, which contains about one-fourth of the organic reaction-product, has not received in the past the attention that it deserves. As triphenylmethane, triphenylcarbinol, and an oil are at times present, an investigation of the cause of the formation of these substances must be made before the reaction, which is evidently a very complex one, can be exactly interpreted." A detailed account of the methods employed by the authors in detecting and separating the above-mentioned products is then given. In my second paper, describing the action of zinc on triphenylchlormethane in acetic ester and the subsequent oxidation of the solution on exposure to air, the following statement is made :[3] "I have been at work for some time trying to determine what becomes of the remaining 20 per cent of the triphenylmethyl. I find some triphenylmethane, triphenylcarbinol, and a portion which cannot be brought to crystallization. It remains, however, to determine whether all these products are formed before or during the oxidation of the unsaturated hydrocarbon." The authors make no reference to these results.

Norris and Culver then describe a series of experiments, from which they draw the following conclusions : "The most evident facts are : First, that much more zinc is used than is called for by Gomberg's equation ; second, that much more oxygen is absorbed than is contained in the peroxide ; and third, that the percentage of peroxide obtained is less than that found by Gomberg."[4]

[1] Ber. d. chem. Ges., **35**, 3919 (1902).
[2] This JOURNAL, **29**, 132 (1903).
[3] *Ibid.*, **25**, 330 (1901).
[4] *Ibid.*, **29**, 137 (1903).

In regard to the first point, it may be said that the method of procedure employed by the authors in their experiments is such as to invalidate the conclusions drawn by them. They say that they found zinc hydroxide as one of the products of the reaction. Of course, the hydroxide could not have been formed in the reaction of zinc upon triphenylchlormethane. It might have come either from the oxidation of some zinc derivative formed in the reaction, or it might have been formed by the direct oxidation of the metal by the oxygen, under the influence of the different products present. If the latter is the case, it is evident that the quantity of zinc entering into the reaction, as found by Norris and Culver, represents really the sum of the quantities entering into two or more reactions. Furthermore, my own experiments, so far as they have gone, show a decidedly simpler relation. Some of the experiments have already been reported,[1] and others are still in progress.[2]

Absorption of Oxygen.

The authors find that much more oxygen is absorbed than is contained in the peroxide. Here again, the conclusion is invalidated because of the formation of zinc oxide. To be of value, the study of the oxidation process should be so conducted as to involve the oxidation of one substance only at a time. My own experiments in this direction were therefore made on pure triphenylmethyl, and it was shown that the unsaturated hydrocarbon takes up about 15 per cent more oxygen than would be required for the formation of the peroxide. Moreover, I also showed what becomes of at least a portion of this excess of oxygen : '' Die Menge des aufgenommenen Sauerstoffs ist demnach grösser als die für die Bildung des Peroxyds erforderliche. Neben dem krystallinischen Peroxyd bildet sich auch ein gelbes Oel, welches ···· 8.83 per cent Sauerstoff enthielt. Es ist ja auch möglich, dass der Verlauf des Oxydationsprocesses von der Natur des gebrauchten Lösungs-

---

[1] Ber. d. chem. Ges., **35**, 3919 (1902).

[2] There is good reason to think that a solution of zinc chloride in acetic ester dissolves metallic zinc. A strip of pure zinc lost in a 10 per cent solution of freshly fused zinc chloride in water only 0.0018 gram in two weeks. In a 10 per cent solution of the same zinc chloride in absolutely pure acetic ester the loss was 0.020 gram in twenty-four hours, 0.035 gram in five days, and 0.066 gram in two weeks. The ester itself had no effect upon the zinc. This product will be studied further.

mittel abhängig ist.''[1]   No reference is made by Norris and Culver to the above-mentioned results.   They were published almost a year and a half ago.

The Yield of the Peroxide.

That the equation,

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C + ZnCl_2,$$
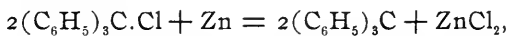
represents the truth in so far as the formation of triphenyl-methyl is concerned, is, I believe, true. But no claim has ever been made that this is, under all circumstances, the only re-action taking place.   As has already been mentioned, I am still looking for such ideal conditions as would insure yields higher than 90 per cent of the theoretical. The yields obtained by me when the solvent employed was acetic ether, were from 75 to 78.5 per cent of the calculated quantity.   Norris and Culver got, at least in one instance, 70 per cent,—not so very far from the yield obtained by myself.[2] The question naturally arises, why did they not get at least a similar yield in the other eight experiments ?   It may be true that '' very slight changes in the conditions of the experiment have a marked influence on the result.''[3]   But when it is intended to draw conclusions from a quantitative study of a reaction, the first requisite is to learn to so control the conditions of the experi-ment as to insure approximately the same yield of the princi-pal product under similar conditions.   Otherwise, the results indicate merely that there is something wrong with the method of procedure.   The yields of the peroxide as obtained by Nor-ris and Culver vary from 29 to 70 per cent.[4]   The question arises, what precautions were taken to insure that the reac-tion was carried to the end ? What precautions were taken to prevent the zinc from becoming coated with a layer of the insol-

[1] Ber. d. chem. Ges., **34**, 2732 (1901).

[2] The experiments in regard to the yield of the peroxide were repeated again. 2.19 grams triphenylchlormethane gave 1.603 grams peroxide, which is equal to 78.8 per cent of the theory ; 2.235 grams gave in another instance 1.575 grams peroxide, *i. e.*, 75.8 per cent of the theory.   But as I have already shown, (Ber. d. chem. Ges., **34**, 2732), pure crystalline triphenylmethyl gives on oxidation only 86.5 per cent of the peroxide; the above percentages indicate the formation of 90.8 and 87 per cent of triphenylmethyl.

[3] This JOURNAL, **29**, 137 (1903).

[4] *Ibid.*, **29**, 137 (1903).

uble triphenylmethylperoxide? Such a layer would prevent the zinc from further action upon the triphenylchlormethane. The authors state that a small yield of the peroxide is always accompanied by a large yield of triphenylcarbinol. There may be, as the authors claim, a certain relation between these two products.[1] Still, as the authors did not assure themselves that the action of zinc on triphenylchlormethane was carried to the end, *i. e.*, that all of the halogen compound was attacked by the metal, and as they treated the reaction-products with water, it is evident that any unchanged triphenylchlormethane would be converted by this treatment into the triphenylcarbinol.

Conclusion.

The claim of Norris and Culver that "the work already done brought to light a number of facts overlooked by Gomberg," cannot, as has been shown, be upheld. The yield of triphenylmethyl, which was somewhat smaller than the calculated, the formation of the double salt of zinc chloride with triphenylchlormethane, the formation of some triphenylmethane, carbinol, and of an oil, when acetic ether is the solvent in the reaction of zinc upon triphenylchlormethane, the absorption of somewhat more than the calculated quantity of oxygen even by the pure triphenylmethyl—these facts have all been discussed in my papers, if not in the first, then in some of the later ones.

In conclusion, the authors say that "where so many reactions are taking place simultaneously there is a chance that there may be subtle changes going on which the experimental data, so far collected, do not lead us to suspect."[2] This, indeed, is a truism and requires no further argument. New facts may be discovered at any time which will make it advisable to assign to the unsaturated hydrocarbon a constitution other than that involving the hypothesis of a trivalent carbon atom —a hypothesis which so far has proved very useful in explaining old facts and suggesting new ones. But from what has

---

[1] I have already shown (Ber. d. chem. Ges., **35**, 3916) that triphenylmethyl can be oxidized to triphenylcarbinol.

[2] This JOURNAL, **29**, 140.

been given in this paper it is evident that the complexity of the reaction, which Norris and Culver attribute to the action of zinc upon triphenylchlormethane, represents in reality the sum of several reactions : (1) The action of the metal upon the halogen compound ; (2) the oxidation of the metal and of the unsaturated hydrocarbon in the presence of several other products ; (3) the action of zinc oxide so formed upon some still unchanged triphenylchlormethane ;[1] and (4) treatment of the reaction-products with water. It has been my aim, in studying quantitatively the action of metals upon triphenylchlormethane, to separate these reactions from each other as much as possible. It was announced in my fourth paper[2] that this phase of the problem is being thoroughly studied and that the results will be published in a later paper.

The acknowledgment by Norris that the experimental evidence put forward by him in the paper of two years ago[3] was, as I showed,[4] faulty, removes from the literature the only experimental evidence that has so far been suggested against the constitution of the unsaturated hydrocarbon as triphenylmethyl.

And as for the "new" facts presented by Norris and Culver, I fully agree with the authors "that none of the facts can be used as evidence against the existence of triphenylmethyl."

ANN ARBOR, MICH., Feb. 14, 1903.

III.—A CONTRIBUTION TO THE CHEMISTRY OF AMERICAN CHEDDAR CHEESE.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

INTRODUCTION.

As cheese ages or ripens, the nitrogen compounds present in the fresh cheese undergo changes in composition more or less profound in character. To the general process that embraces these and other changes is applied the term "cheese

---

[1] I have prepared triphenylmethyl oxide, $(C_6H_5)_3C—O—C(C_6H_5)_3$, from triphenylchlormethane and silver oxide. It will be described in detail later.

[2] J. Am. Chem. Soc., **24**, 628 (1902).

[3] This JOURNAL, **25**, 117 (1901).

[4] *Ibid.*, **25**, 317 (1901).

ripening.'' In a thorough study of the cheese-ripening process, it is of fundamental importance that we ascertain what specific compounds are formed. We must possess such knowledge before we can understand fully in what way different conditions affect the ripening process. The more complete our knowledge is in respect to the various individual compounds formed in cheese-ripening, the better can we understand the causes that produce, and the conditions that control, the process. Whether or not cheese-ripening is in part, or in whole, a biological process, our knowledge of the details of the process must depend very largely upon our knowledge of the specific chemical compounds resulting from such action.

More or less work of a desultory character has been done in this field. Special difficulties are met in the isolation and study of the individual proteolytic compounds found in cheese, owing to a lack of knowledge regarding the chemical constitution of many of them and also to the minute quantities commonly available. Then, too, the same compounds are present or absent according to the conditions of ripening, even in cheese of the same variety. In different kinds of cheese there is still greater variation. Thus far, we have confined our attention to the study of American cheddar cheese, the type most commonly made in this country.

The presence of ammonia was early noticed in cheese. In 1818 Proust[1] discovered in old cheese leucine, which he called '' caseous oxide.'' In 1880 Sieber[2] found tyrosine in a sample of Roquefort cheese. In 1882 Weidmann[3] undertook an investigation of the chemical compounds of Emmenthaler cheese more thorough than had been previously attempted. He was the first to call attention to a product soluble in hot alcohol, called by him '' caseo-glutin,'' which we have recently shown to be unsaturated paracasein lactate.[4] Rose and Schulze,[5] in 1885, were the first to mention the presence of

[1] Ann. chim. phys., [2], **10**, 40 (1818).
[2] J. prakt. Chem., N. F., **21**, 213 (1880).
[3] Landw. Jahrb., **11**, 587 (1882).
[4] This JOURNAL, **28**, p. 429, (1902).
[5] Landw. Versuchst., **31**, 115 (1885).

nuclein in cheese, though their work was largely qualitative. In 1887 Benecke and Schulze[1] added to the list of nitrogen compounds, previously found in Emmenthaler cheese, phenyl-amidopropionic acid. Recently Winterstein and Thöny[2] have reported in Emmenthaler cheese the following compounds : Histidine, lysine, guanidine probably, tetramethylenediamine (putrescine), and pentamethylenediamine (cadaverine). In very few cases do we know anything of the history of the cheese used in the investigations. In our work we are familiar in most cases with the history of the cheese, including the conditions of manufacture and of ripening.

<h2 style="text-align:center">EXPERIMENTAL PART.</h2>

Paranuclein (Pseudonuclein).

In the work first done, about ten years ago, in this laboratory in the study of cheese-ripening, a substance was precipitated by dilute acids from the water-extract of cheese, showing the general chemical behavior of milk-casein toward different reagents. This was called '' soluble casein'' in the absence of knowledge of its specific chemical composition. During the past three years we have given more or less attention to the study of this substance and, though our work is still incomplete, we present here the results obtained up to the present time.

The fact that the substance in question was precipitated by dilute acids, completely by 0.2 per cent hydrochloric acid, suggested its resemblance to Chittenden's so-called casein-dyspeptone,[3] the insoluble substance obtained in larger or smaller quantities when milk-casein is digested with pepsin and hydrochloric acid.

The substance is obtained from cheese by extraction with water and precipitation by hydrochloric acid. We cover about 3 kilograms of finely ground cheese with water, digest it at 55° C. for half an hour, and then decant the extract. The residue is again covered with water, digested, and decanted as before, this operation being repeated several times until the

---

[1] Landw. Jahrb., 1887, 317.

[2] Ztschr. physiol. Chem., **36**, 28 (1902).

[3] ''Studies in Physiol. Chem.,'' Yale Univ., **3**, 66 (1887-8).

extract amounts to 4 or 5 liters. After filtration through ab-
sorbent cotton the solution is cooled to 10° C., or lower, and
allowed to stand until the fat separates on the surface as a
solid layer, which can be readily removed. The solution is then
heated to 50° to 55° C. and treated with enough hydrochloric
acid to equal 0.2 per cent of the solution. The paranuclein
separates as a flocculent, white precipitate, settling to the bot-
tom of the vessel, leaving a supernatant liquid of a bright-
yellow color. The separation of the precipitate may be has-
tened by vigorous stirring. The precipitate is filtered, washed
with water, and then dissolved in 1 or 2 liters of 1 per cent
solution of sodium carbonate. The resulting solution appears
to be complete, though it is milky in appearance. It is fil-
tered, reprecipitated by dilute hydrochloric acid, and the pre-
cipitate is filtered and washed. This process of redissolving
and reprecipitating is repeated three or four times in all.
From this point, two different methods may be employed for
further purification of the substance. By one method, the
third or fourth precipitate by hydrochloric acid is thoroughly
washed with water containing dilute hydrochloric acid, then
with alcohol, and finally with ether, after which it is extracted
by boiling ether for several days, until all traces of fat are re-
moved. It is then dried to constant weight at 105° to 110° C.
for analysis. By the other method, the third or fourth solu-
tion in dilute sodium carbonate is made exactly neutral by
hydrochloric acid, treated with 3 per cent of chloroform to
prevent any bacterial action, and dialyzed in running water
until all chloride is removed. The resulting solution is concen-
trated on the water-bath to a thick syrup, and while still warm
is poured into a mixture of 95 per cent and absolute alcohol.
This is allowed to stand two or three days. A white, gelati-
nous coagulum results, which is filtered, washed thoroughly
with alcohol, placed under absolute alcohol several days,
again filtered, treated with cold ether, then dried, powdered,
and extracted with boiling ether until all fat is removed. It
is then finally dried to constant weight at 105° to 110° C.
This method of dialyzing, concentrating, and then precipita-
ting by alcohol in neutral or alkaline solution appears usually

to carry down with the precipitate large quantities of ash. Jackson[1] has pointed out this fact and has shown that this may be avoided by using the first method given above or by precipitating with alcohol in the presence of dilute acid.

We present in the table below the results of analyses of samples of the substance prepared from different cheeses. The figures given are on the basis of ash-free substance. The first five samples were prepared by dialysis and precipitation by alcohol in neutral or slightly alkaline solution, except sample 3, in which case the solution was probably slightly acid. The other samples were prepared by the first method described above. In samples 6, 7, and 8 the amount of material obtained was not sufficient for making all the determinations.

An examination of the results indicates that we probably did not succeed in freeing the substance from impurities. The few analyses of nuclein on record show considerable divergence. In comparison with Chittenden's casein-dyspeptone, the content of nitrogen, hydrogen, and carbon is lower in our substance, while the sulphur is considerably higher. Chittenden regarded the phosphorus as consisting entirely of calcium phosphate, but Jackson[1] has shown that paranuclein yields over 2 per cent of organic phosphorus, if care is taken to prevent calcium phosphate from being precipitated with the substance and to avoid the formation of inorganic phosphates during ignition. We shall give our attention further to methods of separating paranuclein from cheese in the hope of being able to prepare it free from impurities and studying its decomposition-products.

Paranuclein results from the breaking down of casein or paracasein and is always found in the water-extracts of ripening cheese. The amounts commonly found in cheese under different conditions we shall discuss in a future paper.

Amido Compounds.

In the work, an account of which follows, we planned to isolate such diamido compounds as might be present in the cheese examined. Two different cheeses of the normal Ameri-

[1] Am. J. Physiol., **4**, 170 (1900).

Table I.—Analyses of Preparations of Paranuclein Obtained from Different Cheeses.

		C.	H.	N.	S.	P.	O.	Ash.
1.	Cheese bought in open market, three months old	48.51	6.81	14.14	3.19	2.50	24.95	31.53
2.	" " " " "	48.46	5.67	13.25	2.00	2.23	28.39	23.65
3.	" " four and a half months old	52.01	6.98	14.17	1.65	1.41	23.78	1.44
4.	" " seven months old, interior	50.60	7.00	13.65	1.00	1.33	26.32	16.64
5.	" " " " exterior	50.56	7.70	14.36	0.86	1.52	25.00	20.22
6.	" " one month old	46.72	6.86	15.91	....	....	....	....
7.	" " two months old	47.59	6.90	12.36	....	....	....	....
8.	" " three " "	48.82	7.43	12.98	....	....	....	....
9.	" " four " "	50.56	6.73	12.96	0.83	1.13	27.79	3.10
10.	" " five " "	53.12	6.51	13.68	0.89	0.98	24.82	4.42

can cheddar type were used to furnish material for our work. One was four and a half months old, had been ripened at a temperature of 18° C., and possessed a mild and pleasant flavor. The other was fifteen months old, had been ripened at a temperature of about 20° C., and possessed a somewhat pungent but not disagreeable flavor. In preparing the samples for examination, the cheese was cut into small pieces, the rind being excluded. We used 8 to 10 kilograms of each cheese. After drying in air at room temperature, the cheese was placed in large bottles, covered with 95 per cent alcohol, and digested for several days at room temperature, with frequent agitation. The resulting alcoholic solution, which was of a rich yellow color, was filtered through filter-paper from the insoluble portion, the latter being allowed to drain thoroughly. The insoluble residue was then dried at 60° C., in order to remove all alcohol, and furnished a white, crumbly mass. Most of the fat had been removed by the alcohol, and probably some small proportion of the amido-acid compounds. This white mass was next extracted with several portions of water at 55° C., and the extracts filtered through absorbent cotton until about 25 liters of extract were obtained. This water-extract was treated with tannin in excess, a copious precipitate of caseoses and peptones resulting, which was removed by filtration. The excess of tannin in the filtrate was removed by careful addition of lead acetate, until a drop of the reagent gave no further turbidity, after which the precipitate of lead tannate was filtered and washed with water. The excess of lead in this filtrate was then carefully removed by the addition of sulphuric acid, until a drop gave no additional precipitate, the final traces of lead being removed by hydrogen sulphide. The filtrate from the precipitates of lead sulphate and lead sulphide were united, concentrated to small volume on a water-bath, then made alkaline with barium carbonate, and finally boiled about fifteen minutes in order to remove all ammonia. The solution was then made slightly acid with sulphuric acid, the precipitated barium sulphate removed by filtration, and the filtrate made to contain 5 per cent acid by adding sulphuric acid, after which it was precipitated by

phosphotungstic acid. A heavy crystalline precipitate resulted, which was filtered and washed with 200 cc. of 5 per cent sulphuric acid. The phosphotungstic acid precipitate was then suspended in water and treated with barium hydroxide to remove the phosphotungstic acid in the well-known way. The excess of barium was removed by carbon dioxide, the precipitate filtered and washed. This gave a solution which should contain the hexon bases, *viz.*, arginine, lysine, histidine, and lysatine. For the separation of the first three compounds, the Kossel-Kutscher method was employed, and for lysatine, Siegfried's method. To this solution, diluted to 2 liters and made slightly acid by sulphuric acid, was added a solution of silver nitrate, until a drop of the solution, placed on a white porcelain surface, gave with barium hydroxide the yellow precipitate of silver oxide, thus showing excess of silver nitrate. Then barium hydroxide was added to saturation, which formed a somewhat slimy precipitate, filtering slowly. The precipitate was filtered and washed with a saturated solution of barium hydroxide. The filtrate (Solution A) was worked for lysine, and the precipitate for lysatine, histidine, and arginine. The precipitate was suspended in warm water and the barium carefully removed by means of sulphuric acid and the silver by hydrogen sulphide. The precipitate was filtered, washed with water, and the filtrate made to 1 liter (Solution B).

In Cheese Fifteen Months Old.—In 10 cc. of Solution B the nitrogen was determined and found to be 0.00041 gram, or a total of 0.041 gram in the entire extract. This small amount of nitrogen indicates that arginine, histidine, and lysatine were present in exceedingly minute quantities, if at all. It is possible that the small amount of nitrogen present was due to slight traces of peptones which tannin failed to remove.

Lysatine.

In Cheese Four and a Half Months Old.—To Solution B, obtained as described above, we added just enough barium nitrate to remove all sulphuric acid, filtered and concentrated the filtrate to small bulk. Silver nitrate was carefully added

until the presence of an excess was shown by the usual test, and then a few drops of dilute nitric acid were added. Alcohol was next added and a precipitate began to form, when the addition of alcohol was continued until its volume equaled the volume of the solution. Then a small amount of ether was added, when a crystalline precipitate was formed. This was allowed to stand twenty-four hours and then filtered, washed with ether, and dried over sulphuric acid, yielding a product weighing 2.1 grams. The filtrate was used for separating histidine. This product behaved like Siegfried's lysatine, and ànalysis shows its similarity to that body.

0.202 gram substance gave 0.0565 gram Ag.

0.214 gram substance gave 74.5 cc. N at 22° C. and 746 mm.

	Calculated for $C_6H_{13}N_3O_2HNO_3AgNO_3$.	Found.
Ag	27.51	27.97
N	17.90	17.89

A portion of the lysatine silver nitrate, obtained as described above, was treated with hydrochloric acid and evaporated nearly to dryness, this operation being repeated several times to remove the greater part of the nitric acid. Platinum chloride was then added and the solution evaporated nearly to dryness, when, on addition of alcohol, the platinum salt of lysatine separated. This was filtered, washed with alcohol, and dried over sulphuric acid *in vacuo*. Analysis gave the following results:

0.2414 gram substance gave 0.0835 gram Pt.

	Calculated for $C_6H_{13}N_3O_2H_2PtCl_6$.	Found.
Pt	34.28	34.58

Histidine.

In Cheese Four and a Half Months Old.—The filtrate obtained from the precipitate of lysine, as described above, was carefully evaporated on the water-bath to remove ether and alcohol, and then treated with barium hydroxide until 1 drop of the clear supernatant liquid, added to an ammoniacal solution of silver nitrate, gave no precipitate, thus showing the complete precipitation of histidine. This precipitate was fil-

tered, washed with water, and then suspended in water and treated with hydrogen sulphide to remove silver. After the silver sulphide was filtered, the filtrate was evaporated to dryness, this residue extracted with dilute silver nitrate containing a few drops of nitric acid, and the extract precipitated with ammonia, filtered, and washed with water. This precipitate was next suspended in water, decomposed by hydrochloric acid, the silver chloride filtered and washed, and the filtrate concentrated and allowed to stand several days, when crystals began to separate. After standing a few days longer the liquid was filled with crystals. The crystalline mass was washed with ether and dried over sulphuric acid, *in vacuo*, yielding 4.1 grams histidine.

0.374 gram substance gave 0.1156 gram Cl.

0.2918 gram substance gave 0.532 gram N.

	Calculated for $C_6H_9N_3O_2 2HCl$.	Found.
Cl	31.11	30.93
N	18.42	18.23

Arginine.

In Cheese Four and a Half Months Old.—The filtrate from the histidine precipitate was saturated with barium hydroxide, the precipitate filtered, washed with a solution of barium hydroxide, suspended in water, acidulated with sulphuric acid, and the silver removed by hydrogen sulphide. The entire filtrate contained only 0.085 gram nitrogen, equivalent to 0.255 gram arginine. The amount was too small to obtain a crystalline product, and we are led to conclude that arginine does not exist in appreciable quantities in cheese of this age. Winterstein and Thöny[1] have also reported a similar result in case of Emmenthaler cheese, the age of which, however, they do not state.

Lysine.

Solution A, obtained as described above, was freed from barium by sulphuric acid and from silver by hydrogen sulphide, and the filtrate from these precipitates concentrated to small volume. The solution was made to contain 5 per cent

[1] Ztschr. physiol. Chem., **36,** 28 (1902).

of sulphuric acid and precipitated with phosphotungstic acid. The precipitate was filtered, washed with dilute sulphuric acid, suspended in water, decomposed by barium hydroxide, filtered, and the excess of barium removed by carbon dioxide, the solution then being concentrated to small volume.

In Cheese Fifteen Months Old.—To the solution thus concentrated, alcohol of 95 per cent strength was added in quantity equal to twice the bulk of the solution. Picric acid was then added. On standing twenty-four hours no precipitate appeared. The alcohol was then evaporated, the solution concentrated, and a saturated solution of picric acid added, when crystals began to appear, and increased considerably on standing over night. The crystals were filtered, washed with cold water, recrystallized four times from water, finally washed with ether and dried over sulphuric acid, yielding 9.2 grams (Fraction No. 1).

The filtrate from the first fraction of crystals was further concentrated by evaporation and more picric acid was added, producing a small additional yield of crystals. These were filtered, washed with ether and alcohol, and dried over sulphuric acid, yielding 0.8 gram (Fraction No. 2).

The last filtrate was further concentrated by evaporation, when a slimy precipitate separated. The whole mixture was then shaken with ether in sulphuric acid solution in order to remove all picric acid, after which it was repeatedly boiled with animal charcoal and filtered to remove all coloring-matter. The solution was then reprecipitated by phosphotungstic acid, the precipitate decomposed by barium hydroxide, filtered, and excess of barium removed by carbon dioxide , the resulting solution being concentrated to small bulk by evaporation. Alcohol was added equal in amount to twice the volume of the solution and picric acid carefully added. A crystalline precipitate began to form and increased on standing. After twenty-four hours the crystals were filtered, washed with alcohol, recrystallized three times from water, finally washed with ether and dried over sulphuric acid, yielding 14.1 grams (Fraction No. 3).

The last filtrate was further concentrated by evaporation

and yielded an additional crop of crystals, weighing 0.2 gram (Fraction No. 4).

The crystals contained in Fractions 3 and 4 behaved like lysine and showed, on analysis, a composition corresponding to this compound.

	Calculated for $C_6H_{14}N_2O_2C_6H_2(NO_2)_3OH$.	Found.
N	18.66	19.17
C	38.40	38.18
H	4.53	4.21

On converting this salt to a chloride and estimating the chlorine, the following results were obtained :

0.277 gram substance gave 0.3616 gram AgCl.

	Calculated for $C_6H_{14}N_2O_2 2HCl$.	Found.
Cl	32.39	32.24

In Cheese Four and a Half Months Old.—We obtained 5.4 grams of lysine. A portion recrystallized several times from water gave 18.81 per cent nitrogen, the calculated amount being 18.66 per cent nitrogen.

Tetramethylenediamine (Putrescine).

In Cheese Fifteen Months Old.—Fraction No. 1 of crystals, obtained as described above, resembled tetramethylenediamine in its solubilities, and an analysis showed its identity in composition with this compound.

	Calculated for $C_4H_{12}N_2 2C_6H_2(NO_2)_3OH$.	Found.
N	20.51	20.34
H	3.29	3.48
C	35.16	35.40

On converting this compound to a chloride, the following amount of chlorine was obtained :

0.206 gram substance gave 0.365 gram AgCl.

	Calculated for $C_4H_{12}N_2 2HCl$.	Found.
Cl	44.06	43.76

In Cheese Four and a Half Months Old.—We expected to find putrescine in this cheese as in the other, since arginine, of which it forms a reduction-product, was not found, but we were unable to obtain this compound.

Isolation of Ammonia from Ripening Cheese.

We ground with sand 500 grams of a normal cheddar cheese, ten months old, ripened at 13° C. We extracted this with water at 55° C., precipitated the water-extract with tannin, filtered and distilled the filtrate with steam into a dilute solution of hydrochloric acid. The distillate was evaporated after addition of platinum chloride and the ammonium salt isolated, yielding 8.1 grams of ammonium chlorplatinate. After drying over sulphuric acid the following analytical results were obtained :

	Calculated for $(NH_4)_2PtCl_6$.	Found.
Pt	44.21	44.22

Since we have found in the cheese fifteen months old the volatile base putrescine, it was thought possible that small amounts of this base might distil over when the estimation of ammonia is made by distillation with magnesium oxide, thus vitiating the results in the ordinary method of estimation by increasing the amount of nitrogen obtained as ammonia. In the case of the cheese used and under the conditions of experiment, no such contamination was observable.

Discussion of Results.

Summarizing the results secured by the work embodied in the preceding portion of this paper, we find (1) paranuclein as a common constituent of all cheeses examined by us ; (2) in the younger cheese, which was four and a half months old, the three basic products, lysatine, histidine, and lysine ; and (3) in the older cheese, which was fifteen months old, tetra-methylenediamine (putrescine) and lysine.

In neither case were we able to separate arginine, but in the older cheese we found putrescine, one of the reduction-products[1] of arginine. We did not look for guanidine, but this compound might be expected to be present as the other cleavage-product of arginine, and Winterstein and Thöny have reported its probable presence in Emmenthaler cheese. While there is some reason to believe that lysatine is com-

[1] Ellinger : Ztschr. physiol. Chem., **29,** 334 (1900).

posed of arginine and lysine, the point is not clearly settled, and in our discussion we have not assumed this to be the case.

It is known that lysine yields also pentamethylenediamine (cadaverine) on reduction, and Winterstein and Thöny have reported the presence of the latter compound in an Emmenthaler cheese. They do not give any facts in relation to the history of the cheese used in their work, and we are unable, therefore, to make any comparison with our cheese fifteen months old, in which we found one of the reduction-products of arginine, *viz.*, putrescine. Whether cadaverine might have been formed ultimately we cannot say.

There appears to be good evidence that there is regularly in the cheese-ripening process, in the case of hard cheeses like Emmenthaler and American cheddar, a conversion of primary into secondary amido compounds, and these chemical changes may explain, perhaps, the gradual development of flavor in normal cheese ; in other words, we may find that the changing flavor of cheese as it ages is due, to some extent, to increasing quantities of secondary amido compounds.

In flavor, the older cheese used by us was rather pungent, but not unpleasantly so. It had a high ammonia content, which is a marked characteristic of cheese ripened at temperatures above 15° to 18° C., and which also is a usual accompaniment of a pungent flavor. In cheese ripened in cold storage, where the temperature is usually below 5° C., small amounts of ammonia are formed and the flavor is very mild. We must bear in mind, however, that the presence of mere traces of such compounds as putrescine, cadaverine, and ammonia will not suffice to account for marked abnormal sharpness or other unpleasant quality of flavor in cheese, but that they gradually accumulate and, finally, are present in quantities such that we might expect them to predominate and impart to the cheese mass the flavors peculiar to them.

In cheese, technically known as '' gassy,'' characterized by formation of considerable quantities of different gases, hydrogen forms a part of the gas, so far as examinations that have been made show, and this gas can be regarded as an agent easily capable of favoring the early formation of the reduc-

tion-products that have been found, *viz.*, putrescine, cadaverine, and ammonia.

The subject of cheese flavors is one of complex difficulties, but it is safe to say that these flavors are due to the presence of specific compounds, and any work that shows in cheese the formation and presence of compounds capable of imparting flavors will contribute to the solution of a problem whose details are now little understood.

GENEVA, N. Y., Nov. 20, 1902.

à

ON THE EXISTENCE OF PERCHROMIC ACID.

BY HARRISON EASTMAN PATTEN.

It has been established by A. Bach[1] and confirmed by Baeyer and Villiger,[2] that hydrogen peroxide may contain more oxygen than is required by the formula H_2O_2. Bach maintains that chemical union exists between the excess of oxygen and the hydrogen peroxide to form H_2O_3. Berthelot[3] held to this same explanation. Baeyer and Villiger,[4] on the same basis of fact, claim that the excess of oxygen is merely "dissolved" in the hydrogen peroxide solution in water, giving a solution supersaturated with respect to oxygen.

I have repeated many times a simple qualitative experiment bearing on this discussion, and always successfully. Potassium dichromate is dissolved in water to saturation, cooled to $-16°$ C. by ice and salt, and treated with a 2 per cent aqueous solution of hydrogen peroxide, also at $-16°$. Two actions are observed: (1) A white solid separates from the solution, doubtless a combination of potassium; (2) the solution turns blue. When a cold, saturated, aqueous solution of sodium acetate is added to this solution, the lake color of chromous acetate is at once taken on by the solution. On standing half an hour the green color of chromic acetate appears.

Solid chromous acetate was obtained by treating the blue aqueous solution first formed with cold ether, separating, and

[1] Ber. d. chem. Ges., **33**, 1506 (1900).
[2] *Ibid.*, **33**, 2488 (1900).
[3] Ann. chim. phys., [5], **21**, 176.
[4] *Loc. cit.*

adding solid sodium acetate to the blue ethereal solution. In contact with the ethereal solution, solid chromous acetate is rapidly oxidized to chromic acetate. The electrical conductivity of a strong blue ethereal solution of chromous oxide —as I shall call it—was found to be less than 2×10^{-8} reciprocal ohms at about $0°$ C. This experiment was first carried out January 30, 1902.

It will hardly be maintained that the sodium acetate reduces the " perchromic acid," said to exist in this blue ethereal solution, to the chromous state. It appears unlikely, too, that chromous chromium would exist in a solution supersaturated with oxygen, as Baeyer and Villiger claim. The simplest explanation of the facts is that hydrogen peroxide reduces the chromic acid to the chromous state, and forms a higher oxide of hydrogen. Bach's position, that this higher oxide of hydrogen is combined with the chromous oxide, is tenable to the extent that all solutions are combinations of solute with solvent.

The desirability of analyzing the chromous acetate formed here, I fully appreciate. That it is chromous acetate there can be no doubt. I feel that this reaction should be made known now ; later, if no one else has worked upon it, I shall make the analysis, though the speed with which the acetate changes from chromous to chromic renders this difficult. In all probability the reaction between hydrogen peroxide and potassium permanganate takes the same course as that with potassium dichromate, as Berthelot[1] stated in the first place.

This formation of chromous acetate from the blue aqueous and ethereal solutions of chromous oxide and H_2O_x confirms the existence of an oxide of hydrogen higher than H_2O_2, and renders the existence of perchromic acid extremely doubtful, especially as all electrolytic attempts to prepare it have failed in this laboratory and elsewhere.

CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
MADISON, Oct. 27, 1902.

[1] *Loc. cit.*

REPORT.

The Luminosity of Mantles.

The great increase in the luminosity and the stability of the incandescent gas mantles and their ever-increasing use have directed the attention of many investigators to this subject, and efforts have been made to improve upon the results already obtained and to discover other methods and substances which would produce the same results.

A knowledge of the cause of the luminosity would be of fundamental importance in any investigations undertaken to devise new methods or improve old ones, and in the course of these investigations a number of observations have been made which have led to a very satisfactory explanation of the remarkable luminosity of these mantles. Although it has been known for some years that many refractory bodies emit light, when heated to a high temperature, no successful application was made of these observations, except in the use of the Drummond light, until the introduction of the Welsbach mantle about twelve or fifteen years ago. Berzelius had noticed, in the early part of the nineteenth century, the marked incandescence of certain oxides and supposed it to be due to the high temperature alone. Talbot,[1] in 1835, stated that paper soaked in calcium chloride and burned leaves a white network of ashes, which emits a brilliant light. A few years later Cruickshank patented a cage of fine platinum wires which could be suspended in the flame and be heated to incandescence. He attempted to increase the luminosity by coating the wires with a paste of oxides, but found it impossible to make the oxides adhere. In 1852 Bergmann noticed the incandescence of oxide of thorium, and in 1864 Bahr[2] and Bunsen published the results of an investigation in which it was shown that the oxides of the yttrium group of metals, when heated to incandescence, emit a light of great intensity. In a recent article Auer von Welsbach[3] describes his efforts to obtain a practical mantle and his persistence in the experiments, even after all his financial backing had been withdrawn, the factory closed, and the staff of assistants dismissed. Success finally crowned his efforts, and by the continued work of the skilful chemists employed by the company bearing his name the mantles have reached their present perfection. The explanations, which have been offered, of the cause of the

[1] Phil. Mag., **3,** 114 (1835).
[2] Ann. Chem. (Liebig), **132, 227.**
[3] Chem. News, **85,** 254.

luminosity have been based either on a physical cause, ascrib-
ing it to the temperature alone, or on a physical-chemical one,
in which case it is considered to be due to the catalytic action
of one of the constituents or to an oscillatory oxidation.
Drossbach ascribed the action to a peculiar power which the
ceria possessed of converting heat rays into light rays, while
Westphal called attention to the fact that we are dealing with
a basic and an acidic oxide, and that the peculiar manifesta-
tion of energy was perhaps due to the slow combination of the
two oxides.

Killing[1] has pointed out that the mixtures which have been
used for mantles contain one substance which is capable of more
than one degree of oxidation and that the ceria in the Welsbach
mantle and the chromium oxide in the Sunlight mantle can,
by successive oxidation and reduction, increase the flame
temperature and the luminosity. If this is the only action in-
volved we might expect to find an increased luminosity with
an increase in the proportion of ceria, but Hintz has shown
that the addition, above a certain amount, diminishes the
luminosity, as the following figures show :

Thoria. Per cent.	Ceria. Per cent.	Candle power.
99.5	0.5	11.6
99.0	1.0	17.8
98.0	2.0	15.3
95.0	5.0	10.0
90.0	10.0	2.7

Wyrouboff, Armstrong,[2] and von Welsbach[3] likewise ascribe
the effect to a successive oxidation and reduction.

Bunta[4] considers the effect to be due to catalytic action of
the ceria. The thoria forms a porous oxide which is a poor
conductor, while the ceria forms a dense oxide which is a good
conductor and which has the power to condense the gases on
its surface and produce the intensifying effect, when these
gases combine, over a large surface area.

Among the investigators who have explained the results as
due to the effects of temperature alone, Nernst and Le Chate-
lier have been especially prominent.

Nernst[5] compared the light from the mantle with that from
a black body (electric light), and found that the mantle gave
the most intense light in the yellow and violet portions of the

[1] Jour. f. Gasbeleuchtung, 1896.
[2] Proc. Roy. Soc., **70,** 99.
[3] Chem. News, **85,** 254.
[4] J. Soc. Chem. Ind., 1898, 229.
[5] Physik. Ztschr., 1900, [26], 289.

spectrum and emitted fewer heat rays than other substances at the same temperature.

On account of this action the mantle is heated to a high temperature and emits light in that portion of the spectrum which produces the strongest visible effect. In order to show that the luminosity is not due to the gases with which it is in contact, Nernst heated one mantle by the gas flame and another by the electric current, keeping the two at the same temperature by regulating the resistance, and found no difference in the results, but Bunta denied the justice of entirely excluding catalytic action, in some part of the flame, from the possible causes, as he showed that the mantles could be heated to incandescence if introduced into the cold mixture of gas and air. Le Chatelier[1] says the mantles become as incandescent when heated in the hot products of combustion of the flame as when placed in the burning gases themselves. The proportion of energy radiated as visible rays is very high, and while the absolute amount of energy is less than that of a black body raised to the same temperature, yet the black body under the same conditions and with the same surface area actually reaches a much lower temperature and therefore gives less light. Bunta has found, however, that such widely different bodies as carbon, magnesia, ceria, etc., when heated out of contact with the air, showed very little difference in the amount of light radiated, and Swinton has found that while there was a difference in the ease with which they could be heated in a vacuum, by bombardment, yet the amount of light emitted in the different cases was about the same.

The point raised by Nernst and Le Chatelier has been tested by White, Traver, and Russell,[2] and by Féry,[3] who found that an increase in temperature alone will not suffice to explain the results obtained. White and Russell found that with any one mantle the luminosity did increase with the temperature as Le Chatelier claimed, but if his view is correct a slight change in the composition of the mantle should not cause any marked difference in the result. That there is a considerable difference, not only in the temperature of the mantle and the flame surrounding it, but even in the mantles of different composition, without causing a corresponding change in luminosity, is clear from the determinations made with a carefully calibrated and standardized thermo-couple, which indicated a temperature of $1523°$ on the inside of the mantle at a distance of 1 mm. from its surface, while the mantle itself only reached a tem-

[1] J. Soc. Chem. Ind., 1898, p. 1129.
[2] *Ibid.*, **21**, 1012; Amer. Gaslight J., **74**, 488.
[3] Ann. chim. phys., [7], **27**, 433.

perature of $1373°$.   The following table will show in a marked degree the effect of composition on the luminosity :

	Mantle I.	Mantle II.
	Pure ThO_2.	99.5 per cent ThO_2 and 0.5 per cent Ce_2O_3.
Temperature	$1510°$	$1404°$
Illum. value	1.2 candles	15.7 candles

These facts are in direct opposition to the view of Nernst and Le Chatelier, for, with a temperature $100°$ lower in mantle II., the luminosity is thirteen times greater.   White and Russell consider the ceria to be present as a solid solution in the thoria and to act as a very economical transformer of heat into light.   A mantle made from a mechanical mixture of the oxides increased in luminosity, after some hours, more than one made from the mixed nitrates.   If the mixture was gradually converted into a substance similar to the mantle and if at the same time the luminosity increased, the Le Chatelier theory, which was based on the observation that couples coated with the oxides from mantles attained a higher temperature and gave more light than when coated with any other substance under the same conditions, would appear to be in accord with the facts, but all the experiments made by the authors showed that in every case the one with the lower temperature gave the most light.

Féry has determined the total heat and light rays emitted by black bodies and white oxides, and by the application of the results obtained has been able to offer an explanation which is apparently in agreement with the known facts.   To measure the heat radiations he selected a thermo-couple made of iron and constantan (an alloy of copper and nickel) with a silver plate at the junction.   The couples were mounted in a tube at the point where the rays were brought to a focus by a lens of fluorspar.   The best dimensions of the couple were carefully determined, as was the absorption value of the lens, and a special very sensitive form of galvanometer was used to indicate the small currents set up in the couple.   The determinations were first made in terms of the amount of deviation of the mirror and later reduced to absolute values, using a standard whose value could be determined.   The substance under investigation was molded in the form of a cup and attached to the axle of a motor, revolving about 200 times a minute, so as to become evenly heated by the flame of a blast-lamp.

At the moment when the heat radiation was determined the temperature of the material was recorded by a galvanometer attached to a couple which was in contact with the cup.   One

very interesting fact brought out in these comparisons was the marked difference, in some cases, in the heat radiation when the substance was heated in the oxidizing and reducing flames. The following table will give some idea of the relative values at different temperatures, the figures representing the relative deviation of the mirror :

		900°.	1000°.	1100°.	1200°.	1300°.	1400°.	1500°.	1600°.	1700°
Chromium oxide		138	188	252	334	437	564	710	...	...
Carbon		145	192	250	320	410	520	...	...	...
Platinum		22	30	40	54	72	96	123	152	...
Lime {	Oxid.	12	15	20	26	37	54	86	134	216
	Red.	12	15	20	25	32	42	54	71	90
Magnesia		33	42	52	65	83	106	140	186	204
Lanthanum oxide		33	44	57	76	100	136	180	246	354
Thorium oxide {	Oxid.	28	50	56	78	108	142	184	228	...
	Red.	18	24	30	38	50	69	99	138	...
Cerium oxide {	Oxid.	58	103	172	272	...	...	...	...	...
	Red.	140	200	290	404	...	...	...	...	...
Auer mixture {	Oxid.	50	76	116	166	240	354	490	...	...
	Red.	30	46	70	108	150	208	300	...	...
Electric furnace		122	166	219	287	362	450	561	700	863

The following curves will illustrate the great differences in the case of the oxides which are used in the mantles and show that the radiation in the case of the ceria, when heated in the reducing flame, is even greater than that of the electric furnace or black bodies at the same temperature :
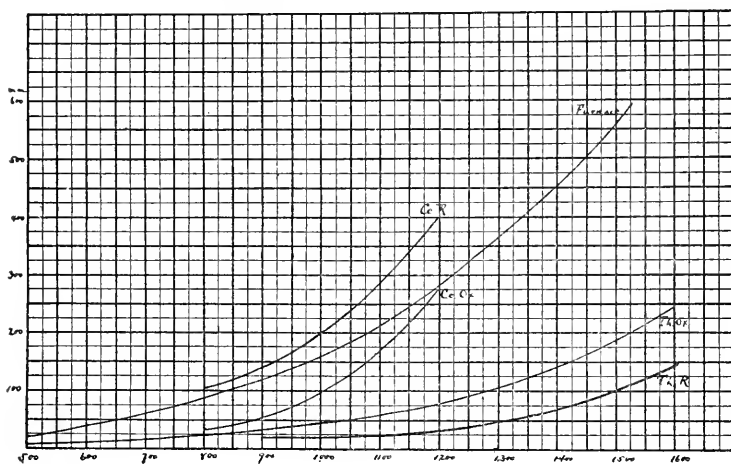
That this result was not due to the oxides of carbon in the flame was shown by heating the material in a hydrogen flame, when the same results were obtained. With the material made from the mantle mixture the results are in their general nature similar to those with thoria, as the radiation is greater in the oxidizing than in the reducing flame.

The results obtained in the measurements of the luminous rays, using an incandescent lamp as a standard and a color screen which cut out all but two green lines, were calculated in terms of the candle power furnished in watts per centimeter according to the temperature. The screen used consisted of two green glasses superimposed, the first, a uranium glass, allowed three brilliant lines to pass, two green and a red, while the second absorbed the red. One of the green lines was quite bright and was the special one by which the eye makes photometric comparisons.

A comparison of these figures shows that while the black bodies, carbon and the electric furnace, radiate very little light, only about 0,005 candle per watt, the oxide of chromium, on the other hand, gives a triple effect, due, no doubt, to the phenomena of luminosity which it exhibits.

Platinum is not suited for use as a mantle on account of its low melting-point, as compared with the substances actually used, while the oxide of lanthanum, which radiates a very large amount of light, rapidly volatilizes in the air.

The Auer mixture furnishes more light in the oxidizing flame than the thoria in the reducing flame, and probably still more in the reducing flame, although the values could not be determined.

The relative intensity of luminosity of mantles made of thoria, ceria, and the Auer mixture is shown by the following values :

	Candle power.
Mantle of thoria	1
" " ceria	7
" " Auer mixture	70

This necessitates some explanation besides the mere condition of temperature produced by the flame. When a Bunsen flame is directed against the sides of a mantle of thoria, the interior blue cone, whose temperature is relatively low, only produces a dark spot on the mantle, but with the ceria a very different result is obtained. A very bright zone starts at the outside and passes towards the center, giving the general effect of particles of potassium nitrate thrown on heated charcoal. This action is repeated again and again, indicating a

Light Radiation at Different Temperatures.

	900°	1000°	1100°	1200°	1300°	1400°	1500°	1600°
Electric furnace	0.0000	0.00014	0.00037	0.0009	0.00214	0.0041	0.0073	0.0135
Corundum	0.00012	0.00026	0.00041	0.0018	0.0051	0.0127	....	....
Carbon	0.00009	0.00025	0.00071	0.00176	0.0035	0.0054	....	....
Chromium oxide	0.00012	0.00037	0.00121	0.00385	0.0086	0.0155	....	....
Platinum	0.0000	0.00064	0.00161	0.00447	0.0107	0.0207	0.0352	0.0521
Magnesia	0.0000	0.00025	0.00062	0.00165	0.00516	0.0127	0.0229	0.0346
Zirconium oxide	0.00024	0.00055	0.00158	0.0051	0.0162	0.0362	0.056	0.0895
Calcium oxide { oxidizing	0.0000	0.00093	0.00233	0.0031	0.00655	0.0149	0.0262	0.0384
{ reducing	0.0000	0.0000	0.00081	0.00129	0.00225	0.00498	0.0197	0.0227
Lanthanum oxide { oxid.	0.00049	0.00304	0.0925	0.0216	0.0435	0.0709	0.0955	0.124
{ red.	0.00028	0.00097	0.00264	0.00762	....	....	....	....
Cerium oxide { reducing	0.0008	0.00112	0.00206	0.00355	....	....	....	....
{ oxidizing	0.00028	0.00016	0.00172	0.00495	0.0119	0.0238	0.0392	0.0556
Thorium " { oxidizing	0.00038	0.00081	0.00186	0.00466	0.0148	0.0350	....	....
{ reducing	0.0000	0.00067	0.00213	0.00618	0.0140	0.0273	0.0438	....
Auer mixture { oxidizing	0.00032	0.00085	0.0055	0.0129	0.0289	....	....	....
{ reducing	0.00070	0.0021	....	....	....	....	....	....

condensation of the gases of the flame and a combination with the excess of air. That the thoria and ceria have a different influence upon the combination of gases has been shown by Bunta, who found that while no difference was observed in the presence of thoria, the ceria, on the other hand, would, in the case of a mixture of hydrogen and oxygen, which in the presence of an inactive substance combines at 650°, cause the combination to take place at 350°. This phenomenon will also explain the high luminosity manifested by the mantle for, on account of the very rapid increase in luminosity with the rise in temperature, the mean ray measured at the mean temperature is greater than the ray which the body would furnish if the temperature were uniform and equal to the mean temperature indicated by the couple.

In studying the photographic prints of the heated mantles of thoria, ceria, and the Auer mixture the author found that the ceria appeared almost black and acted like the black bodies. Further experiments showed that the ceria, when photographed by the illumination of an electric arc, when hot, exhibited a power of radiation similar to black bodies, thus confirming results obtained by other methods.

The observations made during this investigation led to the following conclusions :

The ceria mantle gave no light on account of the reduction of temperature due to its very great power of radiation. It has been shown that the couple coated with the mantle material has a temperature of more than 200° below that of the uncoated couple, and it is also known that the luminosity decreases very rapidly with the decrease in temperature. In order to obtain a satisfactory illuminating effect from the ceria the threads of the material would have to have a very small dimension, as the loss of heat is not as great from small threads as from larger ones, an action the author considers due to the viscosity of the gas rather than to the conductivity of the material.

The thoria acts as a support for the ceria, which, owing to its preparation from the mixture of nitrates of cerium and thorium, is in a very fine, spongy form. On account of its porosity it permits the gases to come in contact with the ceria, which has a catalytic action. Owing to its transparency it permits the rays to pass, end finally its great solidity enables it to keep the ceria in its original position and form. Another property of the thoria which is of great importance here is its very weak power of radiating heat, thus enabling it to heat up the ceria, which radiates very rapidly, to a high tem-

perature, which is still further increased by the combustion taking place through the catalytic action of the ceria.

At the temperature of 1200° the radiation of the thoria is ten times less than that of the ceria, and this difference is probably even greater at the elevated temperature which the mantle acquires in its normal working.

In all the mixtures used for mantles the two substances, a radiating one and a supporting one, have been used.

J. E. G.

REVIEWS.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE, IV. BAND. EINRICHTUNGEN VON ELECTROLYTISCHEN LABORATORIEN, unter besonderer Berücksichtigung der Bedürfnisse für die Hüttenpraxis. Von H. NISSENSON, Director des Central-Laboratoriums der Aktiengesellschaft zu Stolberg und in Westfalen. Mit 32 in den Text gedruckten Abbildungen. Druck und Verlag von Wilhelm Knapp. Halle a. S 1903. pp. 51.

This little monograph discusses briefly certain questions connected with electrolysis, the fundamental laws of applied electricity, and a number of matters essential to electrolytic work, such as sources of current, current regulators, measuring apparatus, etc. The larger part of the work, however, is devoted to the description of laboratories in which electrolytic work is done. These include Aachen, Breslau, Clausthal, Darmstadt, Freiberg, Giessen, Königsberg, Lüttich, Munich, University of Pennsylvania, etc. H. C. J.

BAND V. HERSTELLUNG VON METALLGEGENSTÄNDEN AUF ELEKTRO-LYTISCHEN WEGE UND DIE ELEKTROGRAVÜRE. Von DR. W. PFAN-HAUSER, Fabrikant von Maschinen, Apparaten und chemischen Präparaten für Elektroplattierung, Galvanoplastik, und Metallpolierung. Mit 101 in den Text gedruckten Abbildungen. Verlag und Druck von Wilhelm Knapp, Halle a. S. 1903. pp. 144.

As would be inferred from the title, the work is chiefly of technical importance. Certain of the processes described are, however, of general interest. The ground covered by the monograph can be readily seen by referring to some of the chief headings in the table of contents. The author discusses the physical properties of copper precipitated electrolytically, the preparation of metal powder, the preparation of metal foil, the preparation of wires, the preparation of tubes, electrolytic etching, electrogravure, etc. H. C. J.

QUALITATIVE ANALYSIS. A manual for the use of students in schools and colleges. By L. M. DENNIS, Professor of Analytical and Inorganic Chemistry, and THEODORE WHITTLESEY, Instructor in Analytical Chemistry, Cornell University. Ginn and Co.: Boston. 1902.

This is a new manual. The authors desired " to prepare

a work on qualitative analysis that shall be exact and compendious, avoiding, on the one hand, the diffuseness of the larger treatises, and on the other, the incompleteness of the smaller manuals.'' The very explicit directions for the separation of the elements are followed in each case by discussions of the methods used, their difficulties, and the reasons for preferring these methods, with references to the literature of the subject.

In brief, the book is short enough to use in the average college course, the methods are thoroughly up-to-date, while the discussions raise the book above the mechanical level and will interest the thoughtful student. The reviewer considers it one of the best manuals.

ELEKTRO-METALLURGIE. Die Gewinnung der Metalle unter Vermittlung des elektrischen Stromes. Von DR. W. BORCHERS, Professor der Metallurgie und Direktor des Laboratoriums für Metallhütten-wesen und Elektrometallurgie an der Königlichen Technischen Hochschule zu Aachen. Dritte vermehrte und völlig umgearbeitete Auflage, erste Abtheilung, mit 169 Text-Abbildungen. Leipzig. 1902. Verlag von S. Hirzel.

The new edition of this excellent book is much fuller than the second edition. The first part of the work which has appeared in the third edition deals with the metallurgy of magnesium, lithium, sodium, potassium, aluminium, the cerite metals, copper and nickel. This is less than half the number of metals which will be dealt with when the work is completed, judging from the contents of the second edition.

Any work on the subject of electrometallurgy which comes from Borchers will be accepted as '' standard '' in its field.

H. C. J.

AMERICAN

CHEMICAL JOURNAL

ON THE CATALYTIC DECOMPOSITION OF HYDRO-
GEN PEROXIDE AND THE MECHANISM OF
INDUCED OXIDATIONS.   TOGETHER
WITH A NOTE ON THE NATURE
AND FUNCTION OF CATALASE.

PART I.

BY A. S. LOEVENHART AND J. H. KASTLE.

THE ACTION OF INHIBITORS ON THE CATALYTIC DECOMPOSI-
TION OF HYDROGEN PEROXIDE.

The decomposition of hydrogen peroxide by various sub-
stances, under different conditions, has been the subject of
a large number of investigations.   The theories of oxidation
which have been advanced from time to time have largely cen-
tered around studies upon this peroxide and its catalytic
decomposition, and hence the most important views which
have been held may be here mentioned.   Even in his earlier
work upon hydrogen peroxide, Thénard[1] reached the conclu-
sion that all substances exert some effect on this substance,
some, like the acids, tending to increase its stability, others,
like the metallic oxides and the finely divided metals, tending
to decompose it.   Schönbein made a very careful study of the

[1] Ann. chim. phys., 9, 314 (1818).

catalytic decomposition of hydrogen peroxide and induced oxidations, the results of which he presented in a series of very interesting papers.[1] He pointed out that animal and vegetable extracts from the most diverse sources possess the power of decomposing hydrogen peroxide, and he looked upon this reaction as the prototype of fermentative activity.

Following the work of Schönbein, it was generally believed that all ferments, besides being able to effect their specific reactions, also possessed, in common, the power to decompose hydrogen peroxide. The work of Jacobson,[2] however, indicated that this is not the case. He showed that solutions of enzymes may be made to lose their power of decomposing hydrogen peroxide without losing their specific properties. Spitzer[3] studied the organs of the body with reference to their relative power to decompose hydrogen peroxide, and found them to stand in about the same order as was found by Abelous and Biarnés,[4] and by Salkowski,[5] who measured the oxidation of salicylic aldehyde by these tissues.

From this correlation existing between the power of tissues to decompose hydrogen peroxide and their power to oxidize salicylic aldehyde, Spitzer was led to believe that the two processes have the same cause, and that the power to decompose hydrogen peroxide is, therefore, a true index of the oxidizing power of the tissues. Recently two pieces of work on this catalytic decomposition have attracted much attention. Loew[6] has shown that the decomposition of hydrogen peroxide by plant extracts is not brought about by enzymes in general, but by a specific enzyme of universal occurrence in living organisms, to which he has given the name catalase. Bredig[7] and his pupils have carefully studied the decomposition of hydrogen peroxide by '' pseudo solutions'' of the colloidal

[1] J. prakt. Chem., 1848–1868 ; Pogg. Ann. ; Ztschr. f. Biol., **3**, 140, 325 (1867) ; see also Schaer : Ztschr. f. Biol., **37**, 320 (1899). A good summary of Schönbein's work is given by Bodländer, '' Ueber langsame Verbrennung,'' in Ahren's '' Sammlung chemischer und chemisch-technischer Vorträge,'' 1899.

[2] Ztschr. physiol. Chem., **16**, 340 (1892).

[3] Pflüger's Archiv., **67**, 615 (1897).

[4] Archiv. der Physiologie, [5], **8**, 311 (1896).

[5] Virchow's Archiv., **147**, 1 (1897).

[6] U. S. Dept. Agr. Rept., No. 68 (1901).

[7] Ztschr. phys. Chem., **31**, 258 (1899) ; **37**, 1, 323 (1901).

metals. Quite recently Kastle and Clark[1] have shown that many substances, such as copper sulphate, chrome alum, etc., which have but a comparatively slight effect on the stability of the peroxide at ordinary temperatures, decompose it vigorously at 98°. The cause of the catalytic decomposition of hydrogen peroxide has also been the subject of a good deal of speculation. Thénard[2] was at first disposed to regard the decomposition of hydrogen peroxide by the metals and certain metallic oxides as due to electricity. Later,[3] however, he came to look upon it as an inherent chemical property of the peroxide itself, and associated its instability with that of such compounds as nitrogen trichloride and mercury fulminate. Berzelius,[4] who proposed the term "catalysis" for this and similar phenomena, defined a catalytic agent as one which, "merely by its presence and not through its affinity, has the power to render active affinities which at ordinary temperature are latent." Thus, whereas Thénard considered the decomposition as brought about by chemical forces, Berzelius looked upon it as simply a contact action.

In 1839 De la Rive[5] advanced the theory of alternate oxidation and reduction of the platinum in order to account for its power to induce oxidations. According to this hypothesis, the action of finely divided platinum is analogous to that of nitric oxide in the production of sulphuric acid from sulphur dioxide and air.

The results of Helmholtz[6] and of E. von Meyer[7] have, however, been construed to indicate that De la Rive's hypothesis is untenable. As already pointed out above, Bredig and von Berneck[8] have carefully followed the catalytic decomposition of the peroxide by colloidal platinum, and have found the reaction to conform to the logarithmic equation for reactions of the

first order: $\log \dfrac{1}{1-x} = 0.4343 \, a\theta$. From this they have

[1] This JOURNAL, **26**, 518 (1901).
[2] Ann. chim. phys., **9**, 94, 314 (1818).
[3] *Ibid.*, **9**, 441 (1818).
[4] Jsb., **15**, 237 (1836).
[5] Pogg. Ann., **46**, 489 (1839).
[6] *Ibid.*, **150**, 483 (1873) ; see Hüfner: J. prakt. Chem., [2], **10**, 385 (1874).
[7] J. prakt. Chem., [2], **14**, 124 (1876).
[8] Ztschr. phys. Chem., **31**, 258 (1899).

argued that only one molecule of the peroxide enters into the reaction, and that the reaction should, therefore, be represented by the equation :

$$H_2O_2 = H_2O + O \quad \text{and not} \quad 2H_2O_2 = 2H_2O + O_2.$$
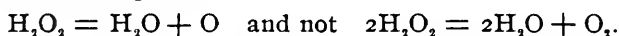
It is evident, however, from the development of the logarithmic equation that it can throw no light on the above question, nor can it show whether the metal enters chemically into the reaction provided it is again liberated during the process. By proving that a reaction conforms to the logarithmic equation, one merely shows that during the process the active mass of only one substance is altered. This is its limitation, and hence the work of Bredig and von Berneck throws no light on the question whether one or two molecules of hydrogen peroxide react, nor does it prove or disprove whether the metal effects the decomposition by undergoing alternate oxidation and reduction, since in this case the active mass of the metal, after the first instant, would remain unchanged throughout.

One of the most interesting observations on the decomposition of hydrogen peroxide by various organic and inorganic catalyzers is that certain substances, especially those of a highly poisonous nature, greatly inhibit the change, even when present in very small quantities. In this connection Schönbein was the first to call attention to the inhibiting action of hydrocyanic acid. He showed, in the most striking way, that hydrocyanic acid prevents the catalytic decomposition of hydrogen peroxide by the leaves of the *Leontodon* and also by the red-blood corpuscles.[1] He reached the conclusion, therefore, that sudden death as the result of hydrocyanic acid poisoning is due to an incapacitation of the red blood corpuscles, as the result of which suffocation is produced. From the fact that hydrocyanic acid inhibits the decomposition of hydrogen peroxide by both platinum and blood, Schönbein thought that the catalytic action of these two substances on the peroxide must be similar.

Bredig and his co-workers[2] have recently made an extensive

[1] Ztschr. für Biol., **3**, 140 (1867).

[2] Bredig and von Berneck : Ztschr. phys. Chem., **31**, 258 (1899) ; Bredig and Ikeda : *Ibid.*, **37**, 1 (1901) ; Bredig and Reinders : *Ibid.*, **37**, 323 (1901).

study of the inhibitory action of many substances on the decomposition of the peroxide by colloidal platinum and gold. In this connection they have pointed out a number of interesting analogies between the colloidal metals and the enzymes, and have even gone so far as to call the colloidal metals "inorganic ferments." They carry the analogy further and speak of the action of inhibitors as "poisoning" the platinum. This analogy between the action of inhibitors on the catalytic decomposition by tissue extracts and by colloidal platinum is considered by them to be a most significant fact. They have shown, however, that in a few instances, substances which had been found not to inhibit the catalytic decomposition by tissue extracts do inhibit the action of colloidal platinum.

On the other hand, our own results on the effect of various substances on the catalytic decomposition of hydrogen peroxide by different substances go to show that this analogy in the action of inhibitors on the catalysis, interesting though it may be, is still a mere coincidence, and that there are a number of substances which act altogether differently on the two orders of catalyzers, *i. e.*, they inhibit the one and accelerate the other.

As to the cause of the inhibitory effect of these several "poisons" on the decomposition of hydrogen peroxide by the colloidal metals, several theories have been advanced by Bredig and Ikeda, the substance of which is as follows:

1. The poison acts on the catalyzer and not on the hydrogen peroxide, at least such is the case with hydrocyanic acid.[1]

2. If it be assumed that for the catalytic decomposition of hydrogen peroxide, the presence of oxygen in the platinum is necessary, either dissolved or chemically united, then the effect of reducing substances, like hydrogen sulphide, hydroxylamine and phosphorus, is easily understood.

3. The surface of the platinum may be chemically or mechanically changed by the deposition of some layer, such as sulphur from hydrogen sulphide, and calomel or mercury from mercuric chloride.

[1] In this connection see also Rauditz: Ztschr. phys. Chem., **37**, 551 (1901).

4. The platinum may be chemically altered or dissolved, for example, by hydrocyanic and hydrochloric acids. The quantity of platinum present, however, is often far in excess of the "poisonous" substances.

5. The surface of the platinum may be so affected that the potential difference between it and the solution, and consequently its surface-tension, may be altered. This might be due to the formation of complex substances (such as $H_2Pt(CN)_4$) or to the removal of oxygen from the surface of the platinum by carbon.

It occurred to us in this connection that perhaps a better idea could be formed of the effect of various inhibitors on the catalytic decomposition of hydrogen peroxide by studying their effect on a number of substances capable of effecting the decomposition.

Accordingly, we have investigated the effect of a number of inhibitors on the catalytic decomposition by the following substances : Finely divided silver, platinum, copper, iron, silver oxide, thallium, ferrous oxide, copper sulphate, and catalase. Among the substances whose effect on the catalysis has been studied may be mentioned the following : Hydrocyanic acid, sodium nitrate, potassium nitrate, sodium chloride, sodium fluoride, sodium sulphate, sodium phosphate, sodium bicarbonate, potassium bromide, potassium oxalate, ammonium nitrate, ammonium chloride, ammonium sulphocyanate, thiourea, urea, hydrogen sulphide, hydroxylamine, phenylhydrazine, acetic acid, and sodium thiosulphate.

In order to determine the effect of these substances on the decomposition of hydrogen peroxide by the various catalyzers above mentioned, the following mode of procedure was adopted. A weighed amount of the catalyzer, usually 0.05 or 0.1 gram, was placed in a salt-mouth bottle, having a capacity of 200 cc. To this 1 cc. of a solution containing a known amount of the inhibitor was added. A small bottle of 6 cc. capacity, containing 5 cc. of 3 per cent hydrogen peroxide, was then carefully placed in an upright position in the larger bottle. The larger bottle was then connected with a gas-burette, and at a given instant the smaller bottle contain-

ing the hydrogen peroxide was overturned and the whole well shaken so as to intimately mix the contents. The solution of the inhibitor was thereby reduced to one-sixth of its original concentration. Readings were then made on the gas-burette at intervals of fifteen seconds. When not stated to the contrary, all observations were made at room temperature ; and, inasmuch as small differences in the quantities of gas are not taken into account in the interpretation of our results, no corrections were made for the effect of temperature and pressure on the volume of the gas. In all of our experiments " Oakland,ˑ3 per cent, Hydrogen Dioxide" was employed. This preparation now goes by the trade name of "Dioxogen." It has been found to be stable under ordinary conditions, very uniform in composition, and to contain no impurities that would interfere with our work. In order to make correction for any slight alteration in the strength of the peroxide solution while in use and for any variation in the temperature of the laboratory, control experiments with 1 cc. of water instead of 1 cc. of the solution of the inhibitors, were always tried at the beginning of every series of experiments with any given catalyzer, and in the event that any given series of experiments occupied us the entire day, several control experiments were tried at different intervals.

The finely divided silver used in our experiments was prepared by precipitating the metal from solutions of silver nitrate with finely powdered magnesium. The precipitated metal was treated with dilute nitric acid to remove small amounts of magnesium. It was then repeatedly washed with large amounts of water and dried at 75°. It was then rubbed in an agate mortar to a perfectly homogeneous powder.

In Table I. are given the results showing the effect of several neutral salts, urea, thiourea, hydrogen sulphide, hydroxylamine, and phenylhydrazine on the decomposition of the peroxide by finely divided silver.[1]

This series of experiments reveals many interesting facts.

[1] In order to see the effect of any substance on the catalysis, compare the number of cubic centimeters of oxygen obtained with the volume of oxygen obtained in the control experiment for the same interval.

Table I.

0.1 gram silver.   5 cc. H_2O_2.   1 cc. water or solution.

Time. Sec.	1. Water.	2. N. NaNO₃.	3. N. NaCl.	4. N/10 Na₂F₂.	5. N. Na₂SO₄.	6. N/2. Na₂HPO₄.	7. N. NaHCO₃.	8. N. KNO₃.	9. N. KBr.	10. N/10 KBr.	11. N/100 KBr.	12. N/50 KI.
15	3.5¹	5.5	0.25	11.0	8.0	4.0	6.0	6.0	0.0	0.0	1.5	0.75
30	6.5	10.0	1.75	14.0	15.0	6.0	8.5	11.0	0.0	0.0	4.0	1.25
45	10.0	14.0	5.00	17.0	22.0	7.5	12.5	13.75	0.0	0.5	7.5	2.0
60	13.0	17.5	9.00	20.0	29.0	9.0	16.0	16.00	0.0	0.5	10.0	3.0
75	15.75	20.5	12.00	22.0	34.0	10.5	19.5	19.00	0.0	0.5	12.0	4.5
90	18.25	22.75	13.50	24.0	37.0	12.0	22.0	21.75	0.0	1.0	14.0	6.0
105	20.00	24.50	15.50	26.0	39.0	13.25	24.5	24.00	0.0	1.5	17.0	7.5
120	21.50		17.00	28.0	41.0	14 5	26.5	25.75	0.0	1 5	19.0	9.0
135	22.75		18.50	29.5	43.0	15.3	28.5	27.50	0.0	2.0	20.75	10.8
150	23.5		20.5	30.5	44.0	16.25	30.25	28.50	0.0	2.0	22.75	12.3

Time. Sec.	13. N. (COOK)₂.	14. N. NH₄NO₃.	15. N. NH₄Cl.	16. N. NH₄CNS.	17. N/5 Thiourea.	18. N/5 Urea.	19. 0.6 N. H₂S.	20. 0.06 N. H₂S.	21. N/10 NH₄OH.	22. N/5 Phenyl-hydrazine acetate.	23. N/5 Acetic acid.
15	5.5	7.0	1.0	1.0	1.5	4.0	0.5	4.0	6.0	1.0	3.0
30	8.5	11.0	1.5	1.0	1.5	7.0	0.5	6.0	16.0	1.5	7.5
45	11.0	14.0	1.5	1.25	1.5	8.5	0.5	8.0	25.0	1.7	12.5
60	13.5	17.0	1.5	1.25	1.5	10.0	1.0	9.8	31.0	2.0	19.0
75	17.0	19.5	1.5	1.25	1.5	12.0	1.0	11.0	35.5	2.4	25.5
90	20.5	21.5	1.5	1.25	1.5	14.0	1.0	12.7	40.0	2.5	30.5
105	23.0	23.0	1.5	1.25	1.5	15.25	1.0	14.3	43.0	2.7	35.0
120	25.5	25.5	1.5	1.25	1.5	16.5	1.0	15.8	44.5	3.0	38.5
135	27.0	28.0	1.5	1.25	1.5	17.8	1.0	17.0	47.0	3.2	41.8
150	29.0	30.0	1.5	1.5	1.5	19.0	1.0	18.2	48.7	3.4	44.0

¹ The numbers given under each column of the table represent the number of cubic centimeters of oxygen evolved in the given time,

The results obtained with the neutral salts indicate that those salts whose constituent acid yields an insoluble silver salt, inhibit the catalytic action of silver. Thus sodium chloride, ammonium chloride, and potassium bromide greatly inhibit, or really in the case of the two latter salts when acting in $N/6$ solution, practically prevent the decomposition by silver. This naturally suggested that the cause of the inhibition of the catalytic decomposition by various substances is due to the formation of an insoluble compound as a result of the action of the inhibitor on the catalyzer, whereby the latter becomes coated over with a thin, inpenetrable film of some insoluble substance. We are, however, apt to think of silver as much too inert to effect the decomposition of such salts as potassium bromide and sodium chloride under the conditions of the experiment.

On the other hand, it was long ago pointed out by Proust[1] that silver coins that had lain for many years under the sea were completely transformed into chloride. Then, too, it should be borne in mind that these metals in a fine state of division are much more active than in their ordinary form, and in this connection it has been observed that when finely divided silver is shaken with a neutral solution of potassium bromide or iodide the solution becomes alkaline to both litmus and phenolphthalein. This could only occur as the result of the formation of the silver halide. By comparing colums 3 and 15 of Table I., it will be observed that ammonium chloride is a much better inhibitor than sodium chloride. This is very satisfactorily explained by the fact that ammonium has less affinity for chlorine than sodium, and hence is much more easily replaced by silver, and therefore forms the insoluble coating of silver chloride much more readily with the sodium chloride. This view is still further strengthened by the fact that sodium fluoride has no inhibitory effect on the decomposition, the explanation being that silver fluoride is soluble. The same reasoning applies to the nitrates, sulphates and oxalates, etc.

The theory of the formation of an insoluble film also ade-

[1] Roscoe and Schorlemmer: "Treatise on Chemistry," Vol. II., Part I, 370, (1886).

quately explains how certain substances, even when acting in very small quantities, prevent the decomposition by much larger amounts of metal than they could possibly combine with.

The fact that potassium iodide (12) does not completely inhibit the catalytic action is explained by the fact that this salt is itself an active catalyzer. Hence the decomposition here noted is due almost, if not entirely, to the action of the salt itself, a fact that must be taken into consideration in all experiments in which this substance was used.

The inhibitory action of hydrogen sulphide (19 and 20) is also readily explained on the supposition that an insoluble film of silver sulphide is formed over the surface of the metallic silver.

The action of ammonium sulphocyanate as an inhibitor is peculiar and full of interest. In the first place it should lend itself readily to the formation of an insoluble coating of silver sulphocyanate. This alone would account for its powerful inhibitory effect. We have found, however, in addition to this, that this substance is very readily oxidized by hydrogen peroxide even in the cold and in the absence of an oxygen carrier, with considerable evolution of heat and the production of acid ammonium sulphate and hydrocyanic acid. Hence the loss of hydrogen peroxide, due to the oxidation of the sulphocyanate, together with the production of hydrocyanic acid, doubtless contributes to its apparent inhibitory effect. The interesting results obtained with this substance led us to try the action of its isomer, thiourea, and to compare this with urea. As seen in column 17, thiourea acts as powerfully on silver as an inhibitor as ammonium sulphocyanate. In this case there was apparently no oxidation, or at least no production of hydrocyanic acid. As yet we have not had time to study its action more fully and hence, at present, we are unable to completely explain its inhibitory effect. It may react with the metal to form a sulphide, or its tautomer may form an insoluble silver compound. Urea, on the other hand, showed only a very slight inhibitory effect, thus indicating that the inhibitory action of thiourea is in some way connected with the sulphur which it contains.

The inhibitory action of phenylhydrazine acetate (22) is very marked, whereas hydroxylamine (21) noticeably accelerates the decomposition. Tanatar[1] has recently studied the catalytic decomposition of hydroxylamine by finely divided platinum. It should be mentioned here that, under the conditions of our work, control experiments showed that there was no decomposition of the hydroxylamine.

In view of the fact that so many substances inhibit the catalytic decomposition of hydrogen peroxide by finely divided silver, the acceleration of this process by many neutral salts, such as the nitrates, fluorides, oxalates, and sulphates of the alkali metals and ammonium (see columns 2, 4, 5, 8, 13, and 14, Table I.), is exceedingly interesting. Obviously it is an altogether different phenomenon from the inhibition and some new factor must enter here. The inhibitor acts upon the catalyzer, whereas, on the other hand, it is probable that the accelerator combines with the hydrogen peroxide to produce very unstable addition-products, upon which the catalyzer can react more readily than upon the hydrogen peroxide alone. In this connection Engler and Nasse,[2] and also Schöne[3] and others, have observed that hydrogen peroxide is slowly decomposed by such salts as the chlorides of sodium, potassium and calcium, and sodium sulphate. Another fact of considerable interest might be mentioned in this connection, and that is, that in almost every case we were able to predict whether a given substance would accelerate or retard the catalysis by metallic silver, by reason of the fact that when treated with water or a solution of an accelerator, such as potassium nitrate or sodium sulphate, the silver was not wetted by the liquid and in part, at least, remained floating on the surface thereof. On the other hand, solutions of inhibitors were found to wet the silver at once, and caused it to sink to the bottom of the liquid, indicating that the surface of the metal had been changed in some way.

[1] Ztschr. phys. Chem., **40**, 475 (1902).
[2] Ann. Chem. (Liebig), **154**, 231 (1870).
[3] *Ibid.*, **193**, 241 (1878).

Table II.—Effect of Hydrocyanic Acid on the Catalytic Decomposition by Silver.

0.1 gram Ag. 5 cc. H₂O₂. 1 cc. water or HCN.

Time. Sec.	1. Water.	2. N/5 HCN.	3. N/10 HCN.	4. N/20 HCN.	5. N/50 HCN.	6. N/100 HCN.	7. N/500 HCN.	8. N/1000 HCN.	9. N/2000 HCN.	10. N/5000 HCN.
15	4.7	1.0	1.5	2.0	3.5	4.0	4.5	4.25	4.0	7.7
30	9.0	1.5	1.5	3.75	5.0	5.5	7.0	7.0	7.5	12.5
45	12.5	1.5	1.75	4.5	6.5	7.0	9.0	9.25	10.0	14.87
60	15.0	1.75	1.75	5.5	7.25	8.0	10.5	11.0	12.0	19.0
75	17.6	1.75	2.0	6.5	8.0	9.0	12.0	12.75	14.0	21.62
90	20.0	2.0	2.5	7.5	9.0	10.0	13.5	14.25	15.5	23.87
105	22.0	2.0	3.25	8.5	10.0	11.0	14.5	16.0	17.0	26.12
120	23.8	2.0	4.5	9.25	10.5	12.0	15.5	17.25	18.5	27.62
135	25.5	2.0	5.5	10.0	11.4	12.9	16.4	19.0	20.0	29.62
150	27.0	2.25	6.25	10.5	12.4	13.5	17.4	20.0	21.25	31.25

Table III.—Silver.

Varying quantities of Ag. 5 cc. H$_2$O$_2$, 1 cc. H$_2$O or solution.

Time. Sec.	1. 0.05 gram Ag. 1 cc. water.	2. 0.1 gram Ag. 1 cc. water.	3. 0.2 gram Ag. 1 cc. water.	4. 0.4 gram Ag. 1 cc. water.	5. 0.05 gram Ag. 1 cc. N/10 KBr.	6. 0.1 gram Ag. 1 cc. N/10 KBr.	7. 0.2 gram Ag. 1 cc. N/10 KBr.	8. 0.4 gram Ag. 1 cc. N/10 KBr.	9. 0.8 gram Ag. 1 cc. N/10 KBr.
15	1.75	3.4	6.0	10.0	0.0	0.5	0.0	0.75	0.75
30	3.2	6.1	11.0	15.5	0.0	0.5	0.0	1.0	2.0
45	4.75	8.5	14.5	19.0	0.0	0.5	0.0	1.75	16.0
60	6.5	10.8	18.0	23.5	0.0	0.75	0.5	5.0	27.0
75	7.8	13.0	21.0	27.5	0.0	0.75	1.0	13.0	32.0
90	9.0	14.8	23.5	30.5	0.0	1.0	1.75	20.0	39.0
105	10.4	16.2	26.0	33.0	0.0	1.2	2.50	25.5	43.0
120	11.6	17.6	27.5	35.0	0.0	1.3	3.25	29.75	47.5
135	13.1	18.7	29.0	37.0	0.5	1.3	4.50	32.75	50.0
150	14.5	19.6	30.5	38.7	0.5	1.5	6.50	35.0	51.4

Table IV.

0.1074 gram silver oxide. 5 cc. H_2O_2. 1 cc. water or solution.

Time. Sec.	1. Water.	2. N/10 Na_2F_2.	3. N. NaCl.	4. N. KBr.	5. N. KI.[1]	6. N. KNO_3.	7. N. NH_4CNS.	8. N/5 HCN.	9. N/10 HCN.	10. N/50 HCN.	11. N/1000 HCN.
15	51.0	52.0	25.0	3.5	7.0	50.0	2.5	2.0	5.5	16.0	39.0
30	59.5	59.5	34.0	7.0	9.5	58.0	3.0	3.5	9.0	25.0	55.0
45	60.0		40.0	8.0	11.5		3.25	4.5	12.0	29.5	58.0
60			44.0	8.5	13.5		3.5	5.75	14.75	32.0	
75			46.0	9.25	14.25		3.75	7.5	17.0	34.0	
90			48.0	10.0	16.5		4.0	8.5	19.5	36.0	
105			49.5	10.5	17.5		4.0	9.75	21.5	37.0	
120			50.5	10.75	19.0		4.0	11.0	23.5	38.25	
135			52.5	11.25	20.0		4.0	12.0	25.5	39.0	
150			54.0	11.50	21.25		4.0	13.0	27.0	39.75	

[1] Liquid contained free iodine and became quite alkaline.

Table II shows the effect of varying quantities of hydro-cyanic acid on silver. So much has been done already on the action of this inhibitor that but little need be said here. However, it will be noted that the hydrocyanic acid, when acting in N/12000 solution, possesses a very definite inhibitory action. It is of interest to note, however, that when acting in N/30000 solution it slightly accelerates the decomposition. A similar result was obtained by Bredig and von Berneck.[1]

The results given in Table III. show the effect of a constant quantity of potassium bromide on the catalysis by increasing amounts of silver, the hydrogen peroxide remaining the same in each experiment. It will be observed that while 1 cc. of N/10 potassium bromide almost completely checked the decomposition by 0.05 or 0.1 gram of silver, it is entirely inadequate to prevent the catalysis by 0.4 gram of silver, its retarding effect with this quantity being very marked only at first.

In the series of experiments given in Table IV, 0.0174 gram silver oxide was used, this being equivalent to the 0.1 gram of silver. The oxide is a much more powerful catalyzer than the metal. These experiments show that inhibitors affect similarly the decomposition by silver oxide and silver, and that they stand in the same order of efficiency. In the case of silver oxide, however, the inhibition is never so complete as in the case of silver. Thus potassium bromide, when acting in N/6 solution, altogether prevented decomposition of the peroxide by silver (Table I., column 9), whereas with the equivalent amount of silver oxide 11.5 cc. of oxygen were liberated in one hundred and fifty seconds. If as observed by Thénard, the oxide had been reduced to silver according to the equation,

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2,$$
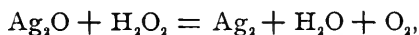
10.4 cc. of oxygen under standard conditions would have been liberated, while the observed uncorrected volume was 11.5 cc. Hence most of the oxygen obtained probably resulted from this reduction.

[1] *Loc. cit.*, Table 29, pp. 330 331.

The effect of these several substances on platinum has also been studied.

The platinum used in our work was prepared by precipitating the metal from a solution of platinum chloride by means of powdered magnesium. It was washed first with dilute sulphuric acid and then with water until the washings contained no sulphate. It was then dried at 85° and rubbed to a homogeneous powder.

0.05 gram of platinum was used in all of our experiments with this metal, otherwise the conditions of the experiments were essentially the same as those on the catalytic decomposition by silver. The results obtained with platinum are given in Table V.

It will be observed that finely divided platinum decomposes the peroxide much more rapidly than silver. It will also be observed that potassium bromide and iodide, and to a much less extent sodium chloride, retard the decomposition. The explanation is probably to be found in the fact that the platinous salts of the halogen acids are also insoluble. An experiment similar to that already described in connection with silver, demonstrated that the addition of finely divided platinum to a neutral solution of potassium bromide or iodide causes the solution to become alkaline. We would, therefore, have produced a thin film of insoluble platinous bromide or iodide over the surface of the metal by the action of this metal on these salts. Such a reaction as this, in which a comparatively inactive metal like platinum replaces a very powerful one like potassium in certain of its compounds, serves to illustrate the effect of the state of aggregation on the chemical activity of the reacting substance.

It will be observed that sodium fluoride does not retard the catalytic decomposition of the peroxide by platinum. While no reliable data are at present available on the solubility of platinous fluoride, we would naturally expect it to be soluble, and hence no protecting film of platinum fluoride would be formed over the surface of the metal.

In their study of the catalytic decomposition of hydrogen peroxide by colloidal platinum, Bredig and Ikeda obtained

Table V.

0.05 gram platinum. 5 cc. H_2O_2. 1 cc. water or solution of substance.

Time. Sec.	1. Water.	2. $N/10$ Na_2F_2.	3. $N.$ $NaCl$.	4. $N.$ Na_2SO_4.	5. $N/10.$ $Na_2S_2O_3$.	6. $N.$ KNO_3.	7. $N.$ KBr.	8. $N.$ KI.	9. $N/5$ HCN.	10. $N/300$ HCN.	11. $N/2000$ HCN.	12. $N.$ NH_4CNS.
15	38.0	44.0	29.0	40.0	32.0	35.0	13.0	24 0	4.0	36.0	40.0	2.5
30	47.0	54.75	42.5	51.5	41.0	43.0	20.0	33.0	6.5	48.0	50.0	3.0
45	49.5	57.5	49.0	57.0	46.0	45.0	24.0	38.0	8.0	51.0	54.9	3.5
60	51.0	57.75	52.0	58.3	49.5	48.5	26.5	42.0	9.0	53.0		3.75
75	53.5		54.0		51.0	51.0	28.0	45.0	10.0	55.0		4.0
90	54.5		55.0		51.75	52.5	31.0	47.0	11.0	56.25		4.0
105	55.25		55.5		52.5	53.0	33.25	48.5	11.75	55 0		4.25
120	55.75		56.0		53.75	53.8	35.0	49.5	12.5			4.4
135	56.0				54.0	54.3	36.4	50.5	13.0			4.5
150	56.0				54.5	54.8	37.5	51.0	13.5			4.75

Time. Sec.	13. $N/5$ NH_4CNS.	14. $N/50$ NH_4CNS.	15. $N/300$ NH_4CNS.	16. $N/5$ Thiourea.	17. $N/50$ Thiourea.	18. $N/5$ Urea.	19. 0.6 N H_2S.	20. 0.006 N H_2S.	21. $N/10$ NH_4OH.	22. $N/5$ Phenyl-hydrazine acetate.	23. $N/5$ Acetic acid.
15	4.0	10.0	30.0	3.0	6.5	32.0	14.0	50	22.0	3.2	32.0
30	6.0	17.0	41.5	4.0	12.0	42.5	28.0	61	38.0	5.0	58.0
45	6.8	22.0	45.5	4.75	16.0	48.0	39.0	62	48.0	6.0	63.5
60	7.5	25.5	49.0	5.75	19.5	51.5	47.0		53.0	6.8	64.5
75	8.25	28.0	51.0	6.5	22.5	53.0	52.0		56.0	7.8	
90	8.75	30.0	52.5	7.5	24.5	54.0	54.5		59.0	8.5	
105	9.2	31.5	53.5	8.0	27.0	55.0	56.0		60.5	9.0	
120	9.5	32.6	54.0	9.0	28.5	55.5	57.5			9.4	
135	9.75	33.8	54.5	9.5	30.0	55.75	58.5			9.8	
150	10.00	35.0	55.0	10.0	31.5	56.0	59.0			10.0	

results quite similar to those given above. They found, for example, that hydrochloric acid inhibited the decomposition, whereas nitric acid accelerated it. In this connection they state : "Es ist also das Cl-ion der Salzsäure welches giftig wirkt. Da dieser auch in Chlorammonium enthalten ist, so zeigt sich dieses physiologisch wohl ziemlich harmlose Salz als ein wirkliches Platingift."[1] They think it likely that hydrochloric acid and its salts act by a formation of chlorplatinic acid, and state that the hydrogen peroxide acts on the hydrochloric acid forming free chlorine. Hence, according to these observers, the "poisoning" of the platinum is due to free chlorine, "which is also a strong poison for organisms." According to our view the inhibiting effects of hydrochloric acid, chlorides, bromides, and iodides depends upon the fact that the platinous halides are insoluble in water and that the platinum becomes covered over with an insoluble film.

Bredig and Ikeda also found that iodine powerfully inhibits the decomposition by platinum. They state that if the effect of the iodine is due to its oxidizing action on the platinum, then bromine should be an even stronger inhibitor. They found, however, that bromine is a much less powerful inhibitor than iodine. This analogy between the platinous and silver halides explains their result, since we should expect platinous iodide to be formed more readily than platinous bromide. Hydrogen sulphide, thiourea, and hydrocyanic acid did not inhibit the action of platinum as much as that of silver. That is what might be expected when we consider how much less readily platinum forms salts than silver.

Bredig and Ikeda found that hydroxylamine hydrochloride markedly inhibits the decomposition by colloidal platinum. As shown in Table V. (21), we found that free hydroxylamine caused some inhibition, but that the metal soon regained its original activity. In fact the decomposition was accelerated towards the close of the experiment.

The fact that in many respects thallium resembles silver, and that certain of the salts of these two metals exhibit analogous properties, rendered it important for our theory to test

[1] *Loc. cit.*, p. 61.

the conduct of this metal toward hydrogen peroxide. The thallous halides very closely resemble the corresponding silver salts in solubility and chemical conduct. Thus the fluorides of both metals are soluble in water, whereas the chlorides, bromides, and iodides of both are insoluble. On the other hand, these two metals display certain striking differences even in their -ous salts. Thus silver cyanide is insoluble in water, whereas thallous cyanide is quite soluble. It seemed, therefore, that with this metal an excellent opportunity was afforded of testing the truth of the ideas set forth above, respecting the action of inhibitors on the catalytic decomposition of hydrogen peroxide by metals.

Accordingly, the decomposition of the peroxide by thallium, acting alone and in the presence of various substances, has been studied. The softness of the metal, together with the fact that it oxidizes so easily on exposure to air, rendered it impossible to make use of the metal in the form of powder. Hence, thin shavings of it were employed, and inasmuch as it was found to break down hydrogen peroxide very slowly at ordinary temperatures, our experiments were performed at 40° C., at which temperature it decomposes the hydrogen peroxide quite actively. The results of our study of the catalytic action of thallium are given in Table VI.

It will be observed that the results reached with this metal are in perfect harmony with the theory, *viz.*, that the inhibition of the catalytic action is caused by the formation of a thin film of some insoluble substance over the catalyzer, this film being formed by the action of the catalyzer on the inhibitor. As shown in Table VI., potassium nitrate (2) and sodium fluoride (11) have no retarding effect on the decomposition, whereas potassium bromide (3 and 4), even when acting in N/60 solution, reduced it to a minimum. And, as was observed in the case of silver, ammonium chloride acted even more powerfully. The formation of the protective film on the surface of the thallium was proven by means of potassium bromide. It was observed that, on introducing a freshly-cut, lustrous piece of the metal in a normal solution of potassium bromide, it at once lost its luster and became covered over

Table VI.

0.1 gram thallium.   5 cc. hydrogen peroxide.   1 cc. water or solution.   Temperature, 40° C.

Time. Sec.	1. Water.	2. N. KNO_3.	3. N. KBr.	4. N/10 KBr.	5. N/100 KBr.	6.[1] 0.83 N HCN.	7. N/10 HCN.	8. N. NH_4Cl.	9. N/100 NH_4Cl.	10.[2] N NH_4NO_3.	11. N/10 Na_2F_2.
15	3.0	5.5	0.75	0.0	1.5	0.5	1.8	0	3.8	2.5	4.0
30	14.0	26.5	0.75	0.5	5.5	1.8	6.0	0	24.0	7.5	19.0
45	29.0	52.0	1.0	0.5	14.0	4.2	12.5	0	50.0	11.8	42.0
60	46.0	59.8	1.0	0.75	28.5	6.0	18.0	0	60.5	15.2	56.8
75	57.0		1.0	1.0	47.0	7.7	25.0	0		18.0	59.6
90	59.0		1.0	1.25	58.0	8.8	31.0	0		20.1	
105	...		1.0	1.3	60.0	10.5	37.5	0		21.5	
120	...		1.0	1.6	...	11.5	43.5	0		22.7	
135							48.5			23.4	
150							52.5			24.4	
165							54.8			25.0	
180							56.0			25.7	

[1] All the metal was dissolved in this experiment except one small piece. Only a small quantity of thallic oxide was noted.
[2] Very little metal left at end of experiment.

with a white, opaque coating, and the solution became alkaline. We see, therefore, that the halides greatly retard the decomposition of hydrogen peroxide by both silver and thallium. On the other hand, the effect of hydrocyanic acid and ammonium nitrate on the catalytic decomposition of the peroxide by these two metals is markedly different. The catalytic power of silver is greatly lowered by the presence of minute quantities of hydrocyanic acid. Whereas, as may be seen from Table VI., column (6), hydrocyanic acid does not prevent the decomposition of the peroxide by thallium even when acting in about $N/7$ solution, and in the presence of $N/60$ hydrocyanic acid a brisk decomposition was observed. That hydrocyanic acid exerts any inhibitory effect whatsoever in the case of thallium is probably due to the fact that in the presence of the peroxide nearly all of the metal is dissolved and thus removed from the sphere of action. So also the retardation of the decomposition observed with ammonium nitrate is probably due to the fact that, in the presence of hydrogen peroxide and ammonium nitrate, practically all of the thallium is dissolved.

A study of the catalytic decomposition by copper and iron was undertaken for the reason that most of the salts of these metals are soluble. The copper used was prepared by sifting zinc dust into a copper sulphate solution and washing the precipitated copper with dilute hydrochloric acid, and then with water, until free from chlorides. It was then filtered and dried at 100 in a current of hydrogen. The iron employed in the experiments was the chemically pure reduced iron of Eimer and Amend.

The effect of inhibitors on the catalytic decomposition by copper and iron is much the same for both, and yet both differ markedly, with respect to the action of inhibitors, from any other metals thus far studied. It has been found, for example, that no substance completely inhibits the action of iron or copper when in the same concentration as employed in the experiments with the other metals.

Potassium bromide, which so powerfully inhibits the decomposition by silver and thallium, was found to have an ac-

Table VII.

Time. Sec.	1. Water.	2. N/10 Na₂S₂O₃.	0.1 gram copper.		5 cc. H_2O_2. 1 cc. H_2O or solution.						
			3. N. KNO_3.	4. N. KBr.	5. 0.6 N. H_2S.	6. N/5 HCN.	7. N. NH_4CNS.	8. N/5 Thiourea.	9. N/10 NH_2OH.	10. N/5 Phenyl-hydrazine acetate.	11. N/5 Acetic acid.
15	3.4	2.5	3.0	4.5	2.5	4.3	3.75	3.0	1.8	4.0	4.3
30	4.8	3.75	4.3	7.0	4.2	6.4	5.0	4.0	2.5	6.0	5.2
45	6.3	4.5	5.5	9.5	5.6	8.25	6.0	4.8	3.0	7.0	6.3
60	7.1	5.5	6.5	12.0	7.0	10.0	6.8	5.8	3.5	7.5	6.9
75	8.3	6.2	7.8	14.0	8.5	11.7	7.8	6.5	4.0	8.0	7.4
90	9.2	6.8	9.0	15.75	9.8	13.7	8.5	7.5	4.5	8.6	7.9
105	10.1	7.7	10.0	17.5	11.0	15.4	9.5	8.3	4.9	9.2	8.4
120	10.9	8.2	11.0	19.0	12.3	17.2	10.2	9.3	5.5	9.5	8.8
135	11.7	8.7	12.0	21.0	13.2	18.0	11.0	10.0	5.9	10.0	9.3
150	12.5	9.3	12.9	22.25	14.1	20.3	11.8	10.8	6.2	10.3	

Table VIII.

0.1 gram iron.   5 cc. H_2O_2.   1 cc. H_2O or solution.

Time. Sec.	1. Water.	2. N. KBr.	3. N. NH$_4$CNS.	4. N/5 HCN.	5.[1] 1 cc. water.	6. N. NH$_2$OH	7. N/5 Phenyl-hydrazine acetate.	8. N/5 Acetic acid.
15	3.7	3.5	1.5	5.8	1.75	1.5	1.5	1.5
30	5.7	5.5	2.0	9.8	2.8	2.0	2.2	2.2
45	7.4	7.5	2.9	13.0	3.5	2.4	3.2	3.0
60	8.9	9.5	3.8	15.9	4.2	2.8	3.7	3.5
75	10.3	11.0	4.4	18.6	5.0	3.2	4.5	4.0
90	11.6	12.8	5.0	20.8	5.6	3.5	5.4	4.5
105	12.9	14.7	6.5	22.9	6.3	3.8	5.9	5.0
120	14.0	16.4	7.0	24.8	6.8	4.1	6.5	5.5
135	15.1	17.8	7.5	26.4	7.5	4.5	7.0	6.1
150	16.1	19.5	8.25	27.8	8.1	4.8	7.5	6.5

celerating effect on the action of both copper and iron. Hydrocyanic acid, which has been found to inhibit the decomposition by all substances previously studied, both organic and inorganic, was found to cause a marked acceleration in the action of copper and iron. This fact was of sufficient interest to warrant further study. In order to bring out to better advantage the accelerating action of hydrocyanic acid, the following experiments were tried at 60° :

Copper.

0.1 gram Cu.   5 cc. H_2O_2.   1 cc. water, or N/10 HCN.
Temperature, 60°.

Time in minutes.	1 cc. water.	1 cc. N/10 HCN.
0.5	13.0	28.0
1.0	32.5	44.0
1.5	42.0	49.8
2.0	46.2	51.9
3.0	50.0	53.0
4.0	51.6	53.1
5.0	52.3	53.1

[1] The reduced iron used in Experiments 5, 6, 7, and 8 had stood exposed to the air for several days, hence the falling off in catalyzing power as compared with that used in Experiments 1, 2, 3, and 4.

Iron.

0.1 gram Fe.   5 cc. H_2O_2.   1 cc. H_2O, or N/10 HCN.
                Temperature, 60°.

Time in minutes.	1 cc. water.	1 cc. N/10 HCN.
0.5	3.8	29.0
1.0	11.5	43.0
1.5	18.3	46.0
2.0	24.0	48.1
3.0	31.2	49.3
4.0	36.1	49.8
5.0	46.3	50.1

These experiments prove that hydrocyanic acid greatly accelerates the decomposition of the peroxide by both copper and iron, especially in the earlier stages of the reaction, the amount of oxygen liberated by the copper in the first half minute being doubled by the presence of the hydrocyanic acid, and in the case of iron the rate of decomposition is increased over seven times.

We have also observed that hydrocyanic acid greatly accelerates the rate of decomposition of hydrogen peroxide by ferrous hydroxide at ordinary temperatures, and at the same time the course of the reaction of hydrogen peroxide on ferrous hydroxide is very materially changed by the presence of hydrocyanic acid. The difference in the two reactions is certainly very striking. On adding hydrogen peroxide to ferrous hydroxide alone, the latter is oxidized to the ferric condition at once with but little or no decomposition of the peroxide. On the other hand, when N/5 hydrocyanic acid is added to the ferrous hydroxide, and then hydrogen peroxide, the mixture takes on the color of Prussian blue, and simultaneously a vigorous decomposition of the hydrogen peroxide occurs. Here the acceleration produced by the hydrocyanic acid is a distinctly chemical effect and is easily explained by the formation of one of the double cyanides of iron, probably Prussian blue, all of which have been found to decompose hydrogen peroxide at ordinary temperatures.

A reaction somewhat similar to this has been observed in studying the decomposition of hydrogen peroxide by copper sulphate at high temperatures. Here, as has been observed

with the ferrous hydroxide, the decomposition of the peroxide is greatly accelerated by hydrocyanic acid, due doubtless to the formation of cupric or cuprous cyanide and its action on the peroxide.   The exact amount of this acceleration may be seen from the following :

Table IX.—Effect of Hydrocyanic Acid on the Catalytic Decomposition of Hydrogen Peroxide by Copper Sulphate at 85° C.

Conditions.	Time. Min.	I. Water. cc.	II. N/10 HCN. cc.	Remarks.
I. 5 cc. N H₂O₂	1	11.5	46.5	
4 " H₂O		...	...	
1 " N/20 copper sulphate	2	24.5	52.5	
II. 5 cc. N H₂O₂	3	32.8	53.5	A light green
1 " N/10 HCN	4	38.5	54.3	flocculent pre-
3 " H₂O		...	...	cipitate is pro-
1 " N/20 copper sulphate	5	42.0	54.3	duced in Exp. II.

It yet remained to test the effect of the inhibitors employed in this investigation on the catalytic decomposition of hydrogen peroxide by catalase. As a convenient source of animal catalase the liver of the hog was chosen. A 10 per cent aqueous extract of the liver was prepared by macerating it thoroughly with coarsely powdered glass, adding the required amount of water, and straining through cloth. In the series of experiments with phenylhydrazine, an extract of liver was employed that had stood over night with toluene. During this interval a coagulum was formed. This was filtered off and the clear yellow extract used in the three series of experiments, the results of which are given in columns 19, 20, and 21 of Table X.

In the other experiments on catalase, the extract of liver was used on the day that it was prepared. The experiments with liver catalase were carried out in the following manner :

One cc. of the liver extract and 1 cc. of water, or of the solution of the substance whose effect on the catalase was to be tried, were placed in the larger bottle. The small bottle,

containing 5 cc. of hydrogen peroxide, was carefully introduced. The large bottle was then connected with the gasburette, and when everything was in readiness, the small bottle was overturned and its contents mixed with that in the larger bottle. The oxygen evolved was then read off at intervals of fifteen seconds until the experiment was brought to a close. In order to obtain comparable results it was found necessary to continually shake the large bottle during the experiment. Loew also found this to be necessary. The experiments were performed at room temperature.

Our results with catalase are given in Table X.

An examination of these results goes to show that the effect of these several substances on the catalytic decomposition of hydrogen peroxide by liver catalase is entirely different from that which they exert on the decomposition by finely divided metals. Catalase resembles silver, platinum and silver oxide, in that hydrocyanic acid (Table X., 17) strongly inhibits its action on the peroxide ; on the other hand, it differs from copper, iron, and thallium in this respect. It resembles platinum also in that potassium bromide (8) does not completely inhibit its action on the peroxide. But it differs in this respect from silver and thallium on the one hand, and from copper and iron on the other, for the reason that this salt completely inhibits the action of silver and thallium, whereas it accelerates the decomposition of the peroxide by copper and iron. Next to hydrocyanic acid, hydroxylamine and the nitrates of sodium, ammonium, and potassium have been found to inhibit the action of catalase to the greatest degree (4, 10, 12, and 18). On the other hand, it has already been pointed out that these substances greatly accelerate the decomposition by silver. Thus hydroxylamine accelerates the action of silver 100 per cent, while it reduces the activity of liver catalase to 1/25 of its original value. Hydroxylamine and the nitrates have been found to have practically no influence on the decomposition of the peroxide by platinum. Similarly thiourea, which accelerates the decomposition by liver catalase, was found to reduce the activity of silver and platinum to 6 and 10 per cent of their former values, respectively.

Catalytic Decomposition of Hydrogen Peroxide.

Table X.

1 cc. liver extract. 5 cc. H_2O_2. 1 cc. water or solution.

Time. Sec.	1. Water.	2. N. NaCl.	3. N. Na_2SO_4.	4. N. $NaNO_3$.	5.[1] N. $NaNO_3$.	6. $N/10$ Na_2F_2.	7. N. $Na_2S_2O_3$.	8. N. KBr.	9. N. KI.	10. N. KNO_3.	11. N. NH_4Cl.
15	27.5	17.0	48.0	8.8	1.0	15.0	48.0	23.0	46.0	7.0	19.0
30	45.0	23.0	59.0	9.2	1.2	29.0	59.0	26.5	57.0	7.4	24.0
45	50.5	28.0	60.5	9.4	1.5	43.0	60.5	28.5	62.0	7.6	27.5
60	58.0	31.0	61.5	9.6	1.7	56.0	61.5	29.5	63.5	7.8	30.0
75	61.0	33.0		9.8	1.8	62.0		30.5	65.5	8.0	31.8
90	62.2	33.8		10.0	2.0	65.0		31.5		8.1	33.0
105	63.8				2.0					8.2	33.5
120					2.25					8.3	34.2
135					2.25					8.4	34.8
150					2.25					8.5	35.0

Time. Sec.	12. N. NH_4NO_3.	13. $N/5$ NH_4CNS.	14. $N/5$ Thiourea.	15. $N/5$ Urea.	16. 0.6 N. H_2S.	17. $N/5$ HCN.	18. $N/10$ NH_4OH.	19.[2] Water.	20. $N/5$ Acetic acid.	21. $N/5$ Phenyl-hydrazine acetate.
15	5.4	2.5	36.0	16.0	2.2	0.75	1.0	20.0	3.8	5.0
30	5.8	2.8	58.0	26.0	4.8	0.75	1.2	28.0	6.3	11.0
45	6.0	3.0	64.0	36.0	7.5	1.8	1.5	32.0	7.8	17.0
60	6.1	3.2		44.0	9.8	3.0	1.8	36.0	9.0	22.0
75	6.2	3.3		51.0	12.2	3.8	2.0	38.0	10.0	27.0
90	6.3	3.6		56.0	15.3	4.2	2.4	40.0	10.5	32.0
105	6.4	3.8		60.0	17.7	5.0	2.5	41.0	11.0	38.0
120	6.4	3.8		62.5	18.0	6.0	2.7	42.0	11.4	42.0
135	6.5	3.8			21.8	6.5	3.0	43.0	11.5	46.0
150	6.5	4.0		21.8	21.8	7.0	3.2	44.5	11.7	48.5

[1] The nitrate and the extract were mixed one hour before the series was taken.
[2] A different extract was used in columns 19, 20, and 21.

It is believed therefore that the facts set forth in the above justify the following conclusions :

1. That various catalyzers are affected differently by different substances,—some of the latter retarding, others accelerating the decomposition of hydrogen peroxide.

2. That the effect of any particular substance on the catalyzer, whether to retard or accelerate its action, can be explained, in the majority of cases at least, upon purely chemical grounds. The action of hydrocyanic acid on ferrous hydroxide in the presence of the peroxide is here cited as a case in point. This, of course, does not apply to the effect of accelerators and inhibitors on catalase. As the nature of this substance is still unknown, so the effect of these several substances upon it must be largely a matter of conjecture.

3. That the inhibitory effect of many substances on the catalytic power of the finely divided metals is due to the formation of a thin insoluble film of a compound of the metal over its surface, this compound being formed by the action of the metal on the inhibitor. This explains why a very small amount of the inhibitor will hold in check a much larger quantity of the metal.

4. Certain substances, like ammonium sulphocyanate, may inhibit the catalytic decomposition for several reasons : First, by being themselves oxidized by the hydrogen peroxide, and thus removing the latter from the solution ; or, secondly, in their oxidation a substance like hydrocyanic acid may be produced which is capable of acting as an inhibitor in a manner already discussed above.

5. That the inhibiting action of various substances on the decomposition of hydrogen peroxide in no way indicates a real analogy between the inorganic and organic catalyzers.

ON THE OXIDATION OF FORMIC ALDEHYDE AND FORMIC ACID BY HYDROGEN PEROXIDE IN THE PRESENCE OF VARIOUS CATALYZERS. THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE AND INDUCED OXIDATION ARE CORRELATED PHENOMENA.

The oxidation of various substances by hydrogen peroxide,

alone and in the presence of various catalyzers and oxygen carriers, has been made the subject of numerous and extended investigations since the discovery of the compound by Thénard. The results reached by Fenton[1] and others, in recent years, in the synthetic oxidation of many organic compounds through the use of hydrogen peroxide, in the presence of ferrous salts, have proved of the greatest possible interest and importance, and yet in spite of all that has been done in these various directions, but little has as yet been accomplished towards arriving at a clear conception of the mechanism of these oxidations.

The simplest view to take of the action of hydrogen peroxide as an oxidizing agent is that in any oxidation it is decomposed into water and active (atomic) oxygen, and that the oxidation is in reality brought about by this latter substance. From this it follows logically, therefore, that any substance that can effect the catalytic decomposition of the peroxide can also bring about oxidations that cannot be effected by hydrogen peroxide alone. The idea that hydrogen peroxide, when it decomposes, gives atomic oxygen as one of the products of decomposition, though an old one, has, as already pointed out above, been again brought forward recently by Bredig and von Berneck[2] in order to explain the results reached by them on the decomposition of the peroxide by colloidal metals.

On the other hand, Traube,[3] in his exhaustive researches on hydrogen peroxide, reached the conclusion that, on heating, the molecules of hydrogen peroxide decompose each other mutually ; that two weakly held hydrogen atoms of 1 molecule of the peroxide split a second into two hydroxyl groups with the result that water is produced, and molecular or passive oxygen set free ; thus, to use his method of representation :

$$\begin{array}{ccc} H & H & H \\ | & | & | \\ O-O & & H \end{array} O_2 \;=\; 2\,H_2O + O_2 .$$
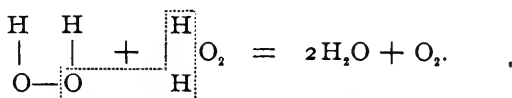
[1] Fenton and Jones : J. Chem. Soc. (London), **77**, 69 (1900).
[2] *Loc. cit.*
[3] Ber. d. chem. Ges., **26**, 1476 (1893).

According to this way of looking at the decomposition of hydrogen peroxide, the mechanism of oxidations effected by means of it, and the accelerating effect of catalyzers on such oxidations, are by no means so easily explained as by the assumption that active oxygen is produced in its decomposition. However this may be, certain chemists have come to see the fallacy of the simpler explanation, and have been led to believe that it is not atomic oxygen produced in the decomposition of the hydrogen peroxide that effects the oxidation of a given substance by the peroxide, but rather the undecomposed portions of the hydrogen peroxide itself.   In this connection Loew[1] states that there is no connection between the power of a substance to decompose hydrogen peroxide and that of causing the oxidation of guaiacum by means of the peroxide, and in support of this conclusion he cites the work of Lépinois,[2] who, two years previously, stated that there is not always a parallelism between the quantities of oxygen developed from hydrogen peroxide by the action of ferments and the intensity of other reactions, such as the oxidation of guaiacum and guaiacol.   On the other hand, the views of Loew and Lépinois are opposed to the results of Spitzer,[3] who found that, with few exceptions, the various tissues decompose hydrogen peroxide in the same order that other investigators (Abelous and Biarnés, also Salkowski) had found them to oxidize salicylic aldehyde.   Spitzer concluded, therefore, that the power of a tissue to decompose hydrogen peroxide is a true index of its oxidizing power.

From certain preliminary observations on the oxidation of certain substances by hydrogen peroxide, the writers of this communication had about reached the conclusion that hydrogen peroxide can only act as an oxidizing agent when it is not being actively decomposed by catalyzers into water and oxygen. In other words, that it is the hydrogen peroxide itself and not the oxygen resulting from its decomposition that effects the oxidation.   It soon became evident, however, that certain substances, if not all, that act as oxygen carriers towards hy-

[1] U. S. Dept. Agr. Rep., **68**, 12 (1901).

[2] Compt. rend. Soc. Biol., 1899, p. 401.

[3] Pflüg. Arch., **67**, 615 (1897).

drogen peroxide also bring about the decomposition of at least a part of the peroxide catalytically, and, vice versa, that most substances, at least, that decompose hydrogen peroxide catalytically can also effect the oxidation of certain substances by means of hydrogen peroxide, that under ordinary conditions are not oxidized by this compound alone.

In order, therefore, to form a better idea of the correlation existing between these processes, it was decided to study the effect of various catalyzers on certain oxidations capable of being effected by hydrogen peroxide. In this connection it occurred to us that possibly the oxidation of formic aldehyde by hydrogen peroxide might prove a suitable one for our purpose, for the reason that it had already been studied by us to some considerable extent,[1] and in some respects, at least, was fairly well understood.

In studying the effect of catalyzers on the oxidation of formic aldehyde by hydrogen peroxide, we made use of a simple piece of apparatus, recently described by Manchot and Herzog.[2] This apparatus, a cut of which is shown in Fig. I., was modified to the extent of using a small, thin-walled glass bottle instead of a flask, and by connecting the stop-cock of the separating-funnel rigidly to a piece of glass tubing (C), thereby enabling us to keep the entire apparatus immersed in a water-bath at any desired temperature, and allowing the two liquids to mix only when they and the entire apparatus had acquired the temperature of the bath. The apparatus was kept immersed in the bath by putting lead weights around the neck of the bottle. Normal formic aldehyde and normal hydrogen peroxide were employed, and, unless expressly stated to the contrary, 5 cc. of each of these solutions were used in each experiment. The formaldehyde was always put in the bottle along with the catalyzer, and the hydrogen peroxide in the separating-funnel. By opening the stop-cock the hydrogen peroxide was allowed to flow down and mix with the formic aldehyde, the duration of the experiment being counted from the moment the two liquids were brought to-

[1] J. Am. Chem. Soc., **21**, 262 (1899).
[2] Ann. Chem. (Liebig), **316**, 321 (1901).
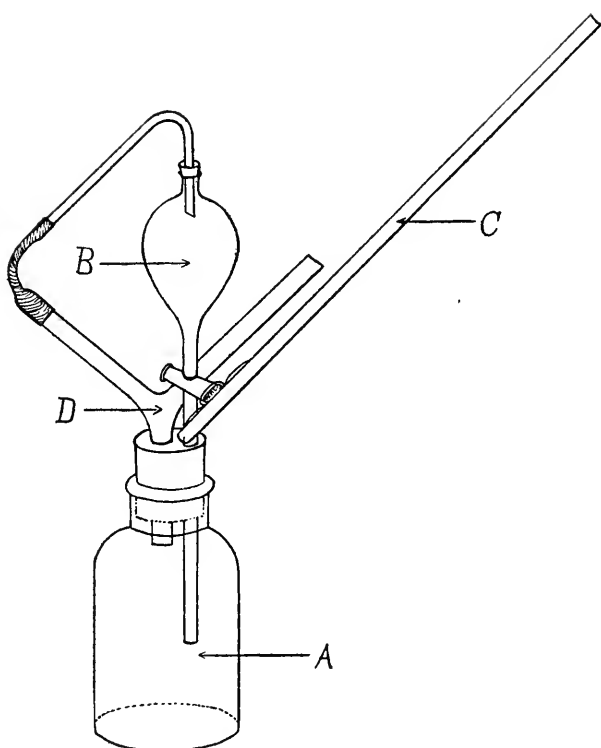
gether.   The apparatus was connected with a gas-burette in
order to measure the amount of any gas produced during the
experiment.   The results of our experiments, together with
the names and amounts of the several catalyzers employed,
and also all other data necessary to a correct understanding of
the work, are given in the following table.   In each experi-
ment 5 cc. of N. hydrogen peroxide and 5 cc. of N. formic
aldehyde were used.   The temperature in every case was 60°
and the duration of each experiment was fifteen minutes.

Table I.

No. of experiment.	Catalyzer.	N/5 NaOH required. cc.	Gas evolved. cc.	Per cent of aldehyde oxidized to formic acid.
1	None	2.1	none	8.4
2	0.1 gram sugar charcoal	2.7	none	10.8
3	0.05 gram platinum black[1]	0.0	57.0	none
4	0.1 gram bone-black	12.2	24.0	48.8
5	0.05 gram platinum black[1]	0.2	54.5	none
6	0.1 gram animal charcoal	11.7	21.0	46.8
7	0.1 " " " 2d specimen	2.3	8.8	9.2
8	0.1 " ferric hydroxide[2]	3.1	22.7	23.6
9	0.1 " ferrous ammonium sulphate	10.10	7.0	66.8
10	0.01 " " " "	7.15	4.0	54.6
11	0.002 gram " " "	1.0	1.0	8.0
12	0.077 " ferric nitrate[3]	20.60	5.0	69.2
13	0.0077 " " "	5.9	9.10	21.0
14	0.0123 " " ammonium alum	3.9	4.0	12.60
15	0.0071 gram ferrous sulphate	19.3	7.0	74.80
16	0.0071 " " "	17.4	7.2	67.2
17	0.00139 " " "	2.55	4.1	10.2
18	0.00278 " " "	4.18	7.4	16.72
19	0.00417 " " "	5.00	5.1	20.0
20	0.00556 " " "	6.85	2.2	27.4
21	0.00695 " " "	17.08	5.7	68.3
22	0.0139 " " "	18.2	2.2	72.8

In looking over the results in Table I., on the effect of various substances on the oxidation of formic aldehyde by hydrogen peroxide, it seemed to us somewhat remarkable that as active a catalyzer as platinum black should have no effect on the oxidation, other than that of causing an apparent retardation. If such were really true, it would seem to support the conclusion that oxidations by hydrogen peroxide are brought about not by any oxygen liberated from the same but by means of the peroxide itself.

[1] All of the hydrogen peroxide was used up in this experiment.

[2] Fe(OH)₃ alone was found not to oxidize formic aldehyde at this temperature.

[3] The acidity of all salts having an acid reaction was determined in every case on the quantity of the salt used in any given experiment, and a correction made on the N/5 NaOH required in each experiment.

However, in this connection, it was observed that platinum black accelerated the oxidation of guaiacum by hydrogen peroxide ; and, further, that just as the catalytic decomposition of hydrogen peroxide is retarded by cold and accelerated by heat, so also the rate of oxidation of guaiacum by hydrogen peroxide in the presence of finely divided platinum was found to be dependent on the temperature, being more rapid the higher the temperature. This plainly indicated that in certain oxidations effected by hydrogen peroxide, platinum black plays the part of an oxygen carrier.

It therefore occurred to us that while formic acid is not oxidized by hydrogen peroxide alone at 60° to 80° C.,[1] it might be oxidized by it in the presence of certain oxygen carriers like spongy platinum, with the result that the formic acid produced by the oxidation of the aldehyde, might itself be oxidized to carbon dioxide and water as fast as formed, thereby completely obscuring the real carrying power of the platinum.

That both formic aldehyde and formic acid are oxidized by hydrogen peroxide under the influence of platinum black, and that formic acid is oxidized to far greater extent than the aldehyde, even when both are present together, may be gathered from the following experiments :

I. 5 cc. of a solution of formic aldehyde were mixed with 5 cc. of N. hydrogen peroxide. 5 cc. of this mixture taken out at once was found to have no increased acidity. This was then mixed with 22.75 cc. N. sodium hydroxide, and to this mixture 50 cc. of 3 per cent hydrogen peroxide were added.[2] After standing for some time this mixture was titrated with N. hydrochloric acid. It took 19.35 cc. N. hydrochloric acid. Hence to calculate the quantity of formic aldehyde present in the original mixture we have 22.75 — 19.35 = 3.4 — 1.2 = 2.2, and 2.2 × 2 = 4.4 cc. N. sodium hydroxide required to neutralize all of the formic acid present. Hence 5 cc. formic aldehyde solution contain 0.1320 gram.

[1] In our earlier work on the oxidation of formic aldehyde by hydrogen peroxide, we proved that formic acid is not oxidized by hydrogen peroxide at these temperatures. J. Am. Chem. Soc., **21**, 262 (1899).

[2] Fifty cc. of the 3 per cent hydrogen peroxide used in these determinations had an acidity equal to 1.2 cc. N. hydrochloric acid.

II. 5 cc. of the solution of formic aldehyde, together with 5 cc. of N. hydrogen peroxide were heated, at 60°, for fifteen minutes. The formic aldehyde remaining unoxidized under these conditions was determined in 5 cc. of the mixture by means of N. caustic soda and 3 per cent hydrogen peroxide with the following results :

Five cc. of the mixture with 50 cc. of hydrogen peroxide and 22.84 cc. N. caustic soda required, at the end of the oxidation, 19.55 N. hydrochloric acid. Hence 22.84 — 19.55= 3.29 — 1.2 = 2.09 × 2 = 4.18 cc. N. caustic soda used to neutralize the formic acid produced by the oxidation of the formic aldehyde remaining in the mixture. Therefore the amount of formic aldehyde remaining in the mixture was 0.1254 gram. Hence 5 per cent of the formic aldehyde was oxidized under the conditions of the experiment.

III. 5 cc. of the formic aldehyde solution, with 5 cc. N. hydrogen peroxide were heated for fifteen minutes at 60° C., with 0.05 gram of platinum black. At the end of this time the mixture was filtered on a dry filter. The filtrate was neutral. The formic aldehyde remaining unoxidized was determined in the manner already described. Found, 0.08592 gram of formic aldehyde. Therefore, 0.04608 gram of formic aldehyde, or 34.9 per cent, had been oxidized under these conditions.

IV. In this experiment 5 cc. of the formic aldehyde solution, together with 5 cc. of N. formic acid and 5 cc. N. hydrogen peroxide, were heated for fifteen minutes at 60° C. with 0.05 gram platinum black. 86.7 cc. of gas were evolved in this experiment, and this gas was found to contain carbon dioxide. At the end of the experiment the mixture was filtered through a dry filter. Five cc. of the filtrate required 2.45 cc. N/5 sodium hydroxide to neutralize, hence the whole required 7.35 cc. of N/5 sodium hydroxide to neutralize the free acid left. The amount of formic aldehyde remaining was determined in the usual manner and found to be 0.1278 gram. Therefore, 0.0042 gram, or 3.1 per cent, of the formic aldehyde had been oxidized under these conditions. On the other hand, 70.49 per cent of the formic acid was oxidized under

these conditions, as may be seen from the following : A mixture like that employed in this experiment of 5 cc. formic aldehyde, 5 cc. of N. formic acid, and 5 cc. of hydrogen peroxide required before the oxidation 24.9 cc. N/5 caustic soda, whereas, after such a mixture had been oxidized it required only 7.35 cc. N/5 caustic soda. Hence, 70.49 per cent of the acid had been oxidized under the conditions of the experiment.

Several interesting conclusions may be drawn from these experiments :

1. That in the absence of formic acid the oxidation of formic aldehyde by hydrogen peroxide is greatly accelerated by finely divided platinum.

2. That, whereas, formic aldehyde is much more easily oxidized by hydrogen peroxide alone than formic acid, the latter is about twice as readily oxidized as the former by hydrogen peroxide when platinum is present ; and that when a mixture of the acid and aldehyde are present in equal quantities with spongy platinum and a quantity of hydrogen peroxide in quantity sufficient to oxidize either but not both, to the next higher state of oxidation, the acid is oxidized almost to the exclusion of the aldehyde.[1]

It was further evident from these results that formic acid would probably prove more useful in studying the effect of various catalyzers on the oxidation by hydrogen peroxide than formic aldehyde. Accordingly, the effect of a number of catalyzers was tried on the oxidation of formic acid by hydrogen peroxide, making use of the apparatus already described. Five cc. of N. formic acid were put in the bottle along with a weighed amount of the catalyzer ; 5 cc. of N. hydrogen peroxide were placed in the separating-funnel. The whole apparatus was then immersed in a water-bath and allowed to come to the temperature of the bath, when the stop-cock was opened and the hydrogen peroxide allowed to mix with the acid and catalyzer, the duration of the experiment being counted from this instant. At the end of a given time, usually

[1] Van 't Hoff also seems to consider formic acid a stronger reducing agent than formic aldehyde, for the reason that it can reduce mercuric oxide, whereas the aldehyde cannot (Vorlesungen über theoretische und physikalische Chemie, 1900, p. 117).

after the lapse of fifteen minutes, the apparatus was removed from the bath and cooled, and, when necessary, the contents filtered on a dry filter. Five cc. of the mixture were then titrated with N/5 caustic soda to determine the loss of acidity due to oxidation, and 1 cc. was titrated with permanganate in order to determine the quantity of hydrogen peroxide consumed in the oxidation. During the experiment the apparatus was usually connected with a gas-burette in order to determine the amount of gas evolved.

The results obtained in this series of experiments, together with all essential conditions of the experiment, are given in Table II.

The effect of the several catalyzers is apparent from the results set forth in the above table. It will be observed that even at 97° C. the oxidation of formic acid by hydrogen peroxide alone amounts only to 5.6 per cent in fifteen minutes, whereas in the presence of small amounts of ferrous salt, copper sulphate, platinum black, and potassium iodide, the oxidation proceeds with great rapidity even at 60° C. It is interesting to note, in this connection, that those substances which exert this accelerating effect on the oxidation also decompose hydrogen peroxide under the same conditions, whereas substances like potassium chloride, which do not decompose the peroxide, do not accelerate the oxidation to any extent. This fact is certainly significant and suggestive, and is brought out in a very striking manner in the case of finely divided gold and platinum. At ordinary temperatures, finely divided gold decomposes a faintly acid solution of hydrogen peroxide very slowly indeed, whereas finely divided platinum effects the decomposition of the peroxide with great rapidity. So in the same way it has been found that at ordinary temperatures finely divided gold scarcely accelerates the oxidation of formic acid by hydrogen peroxide to a measurable extent in twenty-four hours, whereas finely divided platinum under the same conditions brings about the oxidation of 45.2 per cent of the acid present in two minutes. That such is the case may be seen from the following experiments :

I. 0.05 gram gold with 5 cc. N. formic acid and 5 cc. N.

Table II.

No. of experiment.	Catalyzer.	cc. N. Formic acid used.	cc. N. Hydrogen peroxide used.	Time. Min.	Temperature.	N/5 NaOH required.	KMnO₄ used.[7]	Gas evolved. cc.	Per cent oxidation.	Per cent of hydrogen peroxide decomposed.
1	None	5	5	15	60°	24.72	...	none	1.12	none
2[1]	0.05 gram platinum	"	"	"	"	9.5	none	86.2	62.0	100.0
3	0.00139 gram FeSO₄·H₂O	"	"	"	"	24.1	90.5	...	3.92	5.23
4	0.00278 " "	"	"	"	"	23.58	86.0	...	5.68	9.94
5	0.00417 " "	"	"	"	"	21.11	74.0	...	15.56	22.51
6	0.00556 " "	"	"	"	"	18.95	57.0	...	24.2	40.31
7	0.00695 " "	"	"	"	"	17.9	...	...	28.4	...
8	0.0139 " "	"	"	"	"	9.1	...	...	63.6	...
9[2]	0.1 " silver	"	"	"	"	19.5	...	...	22.0	...
10[3]	1 cc. N. KI	"	"	"	"	1.76	...	88.5	92.9	...
11	1 cc. N. KCl	"	"	"	"	24.31	...	0.75	2.8	...
12	None	"	"	"	90°	24.2	...	...	3.2	...
13	0.01 gram CuSO₄·5H₂O	"	"	30	"	12.45	17.5	68.8	50.2	81.67
14[4]	1 cc. 2/5 N. HI	"	"	15	"	19.94	...	9.8	20.24	...
15[5]	0.1 gram copper	"	"	"	97°	10.2	2.0	81.1	59.2	97.90
16	None	"	"	"	"	23.60	84.0	7.2	5.60	12.04
17[6]	0.05 gram gold	"	"	"	"	40.3	35.0	54.0	19.4	63.35
18	" " "	"	"	"	"	20.0	58.5	30.7	20.0	38.74

[1] In Experiments 2, 4, 7, 9, and 10 the gas evolved was found to contain carbon dioxide.

[2] Silver dissolved in the formic acid as the result of the oxidation. This was precipitated by adding 1 cc. of N. HCl. Allowance was made for this in getting the N/5 NaOH required.

[3] A control experiment was tried using 5 cc. N. hydrogen peroxide, 5 cc. of water, and 1 cc. of N. potassium iodide. At the end of the experiment this required 0.2 cc. N/5 NaOH to neutralize it. This correction was introduced into the result of Experiment 10.

[4] In a control experiment with 5 cc. of water, 5 cc. of N. hydrogen peroxide and 1 cc. of 2/5 N. hydriodic acid, for fifteen minutes at 60°C., 0.3 cc. of N/5 NaOH was required to neutralize the acid remaining. This was deducted from the amount of N/5 NaOH required in Experiment 14.

[5] The formic acid dissolved a part of the copper during the experiment.

[6] In Experiment 17, 2 N. formic acid was accidentally used instead of the N. acid.

[7] 1 cc. N. hydrogen peroxide required 19.1 cc. of the solution of potassium permanganate employed in these titrations.

hydrogen peroxide ; temperature 21° to 24° C. ; time, sixteen hours ; 0.25 cc. gas evolved. Required 24.6 cc. N/5 caustic soda, hence 1 per cent oxidation.

II. 0.05 gram platinum, with 5 cc. N. formic acid, and 5 cc. N. hydrogen peroxide ; temperature, 24° C. ; time, two minutes. 76.6 cc. gas evolved. This was found to contain carbon dioxide. Required 13.70 cc. N/5 caustic soda, and 7 cc. potassium permanganate solution. Therefore, 45.2 per cent oxidation and 92.47 per cent hydrogen peroxide decomposed.

The conclusion would therefore seem to be justified that, in general, any substance that can effect the decomposition of hydrogen peroxide can also accelerate oxidations by means of this substance, and that in proportion as a substance is able to break down the peroxide, so also it is able to accelerate oxidations to a corresponding degree. Freshly burned sugar charcoal, for example, decomposes hydrogen peroxide very slowly. It is also a poor oxygen carrier. On the other hand, certain specimens of bone-black decompose hydrogen peroxide rapidly, and these have been found to be good oxygen carriers also.

It has already been indicated above that, if it could be proved that hydrogen peroxide, on decomposition, yields water and atomic (active) oxygen, a very simple and beautiful explanation would be afforded for most, if not all, of the phenomena of oxidation by means of this substance, and also for the accelerating effect of catalyzers on such oxidations. This important point, however, has not as yet been demonstrated. Indeed, as has been pointed out above, quite a number of objections may be urged against it. It occurred to us, therefore, in this connection, that in neutral potassium oxalate we have a substance on which to test this matter experimentally, inasmuch as it has already been proved by Traube[1] that neutral potassium oxalate is not oxidized by boiling with an excess of hydrogen peroxide, whereas on electrolysis in aqueous solution it is vigorously oxidized at the anode.

[1] Ber. d. chem. Ges., **26**, 1476 (1893).

In view of this interesting observation, it occurred to us that it would be of some importance to test the conduct of the oxalate towards hydrogen peroxide in the presence of platinum black and liver catalase, as oxygen carriers.

Accordingly, a solution of neutral potassium oxalate was prepared containing 18.4280 grams per liter. Ten cc. of this solution were found to require 19.85 cc. of N/10 potassium permanganate. With this solution the following experiments were tried :

I. 10 cc. of the potassium oxalate solution, with 5 cc. of water and 10 cc. of the 3 per cent hydrogen peroxide,[1] were allowed to stand fifteen minutes at ordinary temperature, at the end of which time the mixture was found to be neutral. The oxalate remaining in the solution was determined in 10 cc. of the solution by precipitating with calcium chloride, filtering, and titrating the calcium oxalate with N/10 potassium permanganate. It required 8.1 cc. N/10 permanganate. Therefore, the whole of it required 20.25 cc. N/10 permanganate.

II. 10 cc. of the solution of potassium oxalate, with 5 cc. of water, 10 cc. of hydrogen peroxide and 0.05 gram platinum black. Time and temperature, the same as in Experiment I. On adding the platinum a vigorous decomposition of the peroxide took place. The oxalate remaining at the end of this experiment was determined as in I., and was found to require 19.25 cc. N/10 permanganate. The solution was found to have an alkalinity at the end equal to 0.25 cc. N/10 caustic soda.

III. 10 cc. solution of potassium oxalate, with 5 cc. 10 per cent extract of hog liver and 10 cc. of hydrogen peroxide. Time and temperature, the same as in Experiment I. On adding the extract of liver a vigorous decomposition of the peroxide occurred. At the conclusion of the experiment the solution was found to be very faintly acid. The oxalate remaining was determined as in Experiments I. and II. It required 20 cc. N/10 permanganate. In this connection it was observed that the liver catalase was not destroyed, or even materially weakened, by standing for some time in contact

[1] The hydrogen peroxide used in these experiments was neutralized with caustic soda before using.

with the amount of potassium oxalate employed in these experiments.

IV. In this experiment the same quantities of substances were employed as in Experiment I., the only difference being that in this experiment the mixture was boiled for five minutes. The solution was then cooled and the amount of oxalate remaining at the end of the experiment was determined as indicated above. 19.6 cc. N/10 permanganate were required.

V. In this experiment the same conditions were observed and the same amount of substances employed as in Experiment IV., except that 0.05 gram of platinum was added to the boiling solution. A very vigorous decomposition of the hydrogen peroxide occurred on adding the platinum. The solution was then filtered, and the oxalate remaining in the clear filtrate was determined in the manner already described. 19.4 cc. N/10 permanganate were required.

It is evident, from the results of these experiments, that platinum black and liver catalase are unable to effect the oxidation of neutral potassium oxalate by hydrogen peroxide. Now bearing in mind the observation of Traube, that neutral potassium oxalate is oxidized by the oxygen liberated at the anode in electrolysis, that is, by active (atomic) oxygen, it would seem from the results reached in the above experiments, that the oxygen liberated from hydrogen peroxide by platinum and catalase is not atomic but molecular oxygen, and that, therefore, it is incorrect to represent the decomposition of the peroxide by the equation

$$H_2O_2 = H_2O + O,$$
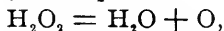
even though the decomposition be one of the first order.

STATE COLLEGE OF KENTUCKY,
January 15, 1903.

EQUILIBRIUM IN THE SYSTEM COMPOSED OF SODIUM CARBONATE, SODIUM BICARBONATE, CARBON DIOXIDE, AND WATER.

BY HERBERT N. McCoy.

The conversion of dry sodium bicarbonate into the normal carbonate, water, and carbon dioxide requires but a very

moderate degree of heat. Complete decomposition takes place rapidly at 100° to 110°.[1] Gautier found that no loss of weight occurs when the salt is placed in a vacuum at 25°. At 35° an appreciable loss had occurred at the end of four days.

Solutions of sodium bicarbonate are far less stable than the dry salt. Rose[2] observed that a solution of sodium bicarbonate loses carbon dioxide by evaporation and leaves nearly pure normal carbonate. The same change was found to occur, at ordinary temperature, when the solution was allowed to evaporate under such conditions that the carbon dioxide given off could be absorbed by caustic potash. Magnus[3] found that carbon dioxide is removed from a solution of sodium bicarbonate at ordinary temperatures by a stream of hydrogen, and Marchand[4] obtained a similar result by drawing air through a saturated solution of sodium bicarbonate at a temperature of 0°. At 38° Marchand found that about 95 per cent of the bicarbonate was converted into normal carbonate, after drawing a rather large volume of air through the solution, and concluded that the change would be complete after sufficiently prolonged action of the air.

Dibbits[5] has pointed out the errors in the determination of the solubility of bicarbonates arising from a failure, on the part of previous experimenters, to prevent loss of carbon dioxide. In his own work on such determinations the loss of carbon dioxide was reduced to a minimum by working in closed vessels which were nearly filled by the solutions. In connection with this work Dibbits determined roughly the pressure with which carbon dioxide is evolved by saturated solutions of sodium and potassium bicarbonates at several temperatures. He obtained the following results with sodium bicarbonate.

Table I.

Temperature.	Pressure, in mm. of mercury.
15°	120
30°	212
40°	356
50°	563

[1] Gautier : Ber. d. chem. Ges., **9**, 1434 (1876).
[2] Pogg. Ann., **34**, 158 (1835).
[3] *Ibid.*, **40**, 590 (1837).
[4] J. prakt. Chem., **35**, 3°9 (1845).
[5] *Ibid.*, [2], **10**, 417 (1874).

Treadwell and Reuter,[1] in connection with another problem, made a few determinations of the composition of a sodium bicarbonate solution, of decinormal strength, when the partial pressure of the carbon dioxide was varied between 2 and 4 per cent of one atmosphere. They concluded that the bicarbonate lost carbon dioxide at reduced pressures, but made no attempt to study equilibrium conditions.

The consequence of a loss of carbon dioxide by solutions of sodium bicarbonate, in connection with analyses of carbonates and bicarbonates and of gases containing carbon dioxide, have, at times, been understood and taken into account. Thus Lunge[2] takes precautions to prevent loss of carbon dioxide from mixtures of carbonates and bicarbonates previous to and in the course of analysis. Lunge and Zeckendorf,[3] and also Rosenthal,[4] recognize the dissociation of sodium bicarbonate in aqueous solution as the cause of the incomplete absorption of traces of carbon dioxide by solutions of sodium carbonate. On the other hand, the change, during analysis, of sodium bicarbonate into normal carbonate was observed by Cameron[5] without, at the time,[6] the true cause being discovered.

The loss of carbon dioxide by solutions of bicarbonates is the necessary consequence of four things : (1) The weakness of carbonic acid, as an acid ; (2) the acid nature of sodium bicarbonate ; (3) the ready dissociation of carbonic acid into water and carbon dioxide ; (4) the comparatively slight solubility of carbon dioxide in water.

The hydrolytic dissociation of sodium bicarbonate is represented by the equation :

$$NaHCO_3 + H_2O \rightleftarrows NaOH + H_2CO_3.$$

The carbonic acid existing thus in solution will necessitate a certain gaseous pressure of carbon dioxide, the ratio of the concentrations in the two phases being simply the solubility,

[1] Ztschr. anorg. Chem., **17**, 202 (1898).

[2] Ztschr. anal. Chem., **37**, 689 (1898).

[3] *Ibid.*, **36**, 329 (1897).

[4] *Ibid.*, **36**, 333 (1897).

[5] This JOURNAL, **23**, 473 (1900).

[6] The more recent work of Cameron and Briggs (J. Phys. Chem., **5**, 537) is discussed later.

as Ostwald uses the term. In a system composed of dilute sodium bicarbonate and vapor, the concentration of the carbon dioxide in the vapor must, therefore, be a direct measure of that of the free carbonic acid in the solution. It might seem then, at first thought, that by measuring the concentration of the carbon dioxide in the vapor in equilibrium with a solution of sodium bicarbonate of known strength one would be able to determine the degree of hydrolytic dissociation of the salt.[1] But the equilibrium in the system in question must be more complex than is indicated by the above equation, as the following considerations show: The immediate result of the action of water on the bicarbonate is doubtless the formation of some sodium hydroxide and free carbonic acid. This action would naturally be expected to reach a state of equilibrium by reason of the reverse reaction. However, the bicarbonate is itself an acid and can act upon the free sodium hydroxide, forming water and the normal carbonate, thus:

$$NaHCO_3 + NaOH \; \rightleftarrows \; Na_2CO_3 + H_2O.$$
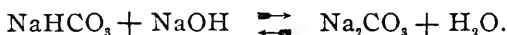
This last equation is really that of the hydrolytic dissociation of sodium carbonate. Though carbonic acid is much stronger, as an acid, than sodium bicarbonate, the relatively great concentration of the latter, as compared with the former, makes it necessary to consider the quantitative effect of the action of this acid salt on the sodium hydroxide produced by the primary hydrolysis.

The equilibrium in aqueous solutions of sodium bicarbonate is, therefore, governed by the two reactions just discussed, each of which represents the hydrolytic dissociation of a salt of a weak acid and a strong base. Walker has shown[2] that for dilute solutions the product of the concentrations of base and acid divided by that of the salt is a constant. It is well known that the same relationship governs the hydrolytic dissociation of salts of strong bases and weak acids,[3] it being presupposed that both the salt, and in the latter case, the base, are highly ionized and to practically the same extent.[4]

[1] See page 450.

[2] Ztschr. phys. Chem., **4**, 324 (1889).

[3] Van 't Hoff : Vorlesungen über theoretische und physikalische Chemie, **I**, 124 (1901).

[4] Arrhenius : Ztschr. phys. Chem., **5**, 17 (1890).

From the reaction

$$NaHCO_3 + H_2O \; \xrightleftharpoons \; NaOH + H_2CO_3,$$
$$\qquad C_1 \qquad\qquad\qquad C_3 \qquad C_4$$

where C_1, etc., represent concentrations in gram-molecules per liter, we have

$$C_3 C_4 = K_1 C_1 ; \qquad (1)$$

and from

$$NaHCO_3 + NaOH \; \xrightleftharpoons \; H_2O + Na_2CO_3$$
$$\quad C_1 \qquad\quad C_3 \qquad\qquad\qquad C_2$$
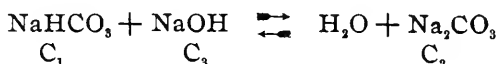
we have

$$C_1 C_3 + K_2 C_2 ; \qquad (2)$$

K_1 and K_2 being the dissociation constants. From (1) and (2)

$$\frac{C_1^2}{C_2 C_4} = \frac{K_2}{K_1} = K. \qquad (3)$$

K is the equilibrium constant for the system under consideration.

In a paper entitled "The Solubility of the Alkali-earth Carbonates in Water Containing Carbon Dioxide,"[1] Bodländer has worked out in a different way from that given above, the equation governing the equilibrium in the reaction,

$$2HCO_3' = CO_3'' + H_2O + CO_2,$$
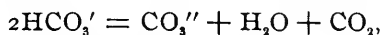
where HCO_3' and CO_3'' refer to ionic concentrations. He gives

$$(HCO_3')^2 = CO_3'' \times CO_2 \times a \text{ constant.}$$

This equation and (3) are practically identical for dilute solutions, where one may neglect the factors for ionization. Bodländer applied this equation to the experiments of Schloesing[2] on the solubility of the carbonates of calcium and barium in water containing carbon dioxide, and to those of a similar nature of Engel[3] on magnesium carbonate. Good results were obtained for the equilibrium constant. In the last paragraph

[1] Ztschr. phys. Chem., **35**, 32 (1900).
[2] Compt. rend., **75**, 1552 ; **75**, 70 (1872).
[3] *Ibid.*, **100**, 352, 444 (1885).

of this paper Bodländer shows that the cause of the increased solubility of sodium bicarbonate in water, when shaken with air, is due to loss of carbon dioxide and consequent formation of sodium carbonate. The calculated increase of solubility agrees approximately with the observed value. The discussion regarding the carbonates of sodium is brief and no reference is made to other work on this subject.

In equation (3) C_4 may be expressed in terms of the partial pressure, P, of the carbon dioxide and a constant, k, whose value depends upon the solubility of carbon dioxide in water, thus :

$$C_4 = kP.$$

According to Just,[1] 1 liter of water at 25° dissolves 0.8256 liter of carbon dioxide measured at 25° and 760 mm. The concentration of such a solution is, therefore, 0.0338 normal molecular.

$$C_4 = 0.0338 \ P.$$

C_1 and C_2 may readily be expressed in terms of a single variable. Let 1 gram-molecule of sodium bicarbonate be dissolved in the volume, V, of water. Let x represent the number of gram-molecules of sodium bicarbonate after equilibrium has been reached. $1 - x$ is the number of gram-molecules of bicarbonate changed into carbonate, and $\frac{1}{2}(1 - x)$ is the number of gram-molecules of carbonate formed.

As is shown on page 452, the concentration of the hydroxide formed is so minute that it may be left out of consideration in this connection. Its maximum amount did not exceed 0.2 per cent of either x or $1 - x$ for the solutions studied.

$$C_1 = \frac{x}{V}. \qquad C_2 = \frac{\frac{1}{2}(1 - x)}{V}.$$

Therefore

$$\frac{C_1^2}{C_2 C_4} = \frac{2x^2}{0.0338 \ PV \ (1 - x)} = K.$$

Calling the concentration of the sodium in gram-atoms per liter C, we have

[1] Ztschr. physiol. Chem., **37**, 342 (1901).

$$C = \frac{1}{V};$$

the equilibrium equation then becomes

$$\frac{2x^2\, C}{0.0338\, P\, (1 - x)} = K.$$

The present work was undertaken with the view of testing the correctness of these deductions. After the experiments had been started a paper appeared[1] by Cameron and Briggs under the title : '' Equilibrium between Carbonates and Bicarbonates in Aqueous Solution.'' The authors drew air through aqueous solutions of the bicarbonates of sodium, potassium, and magnesium of various concentrations, and at four different temperatures, and determined by analysis the proportions of carbonate and bicarbonate after equilibrium had been reached. It is rather remarkable that no reference is made, in their paper, to any previous record of loss of carbon dioxide by bicarbonate solutions. Inasmuch as no quantitative application of the law of mass-action to this equilibrium was attempted by Cameron and Briggs, the work here reported was continued.

The experimental problem presented was the determination of the composition of the liquid and vapor phases in equilibrium with one another at constant temperature, for various proportions of the constituents. The temperature chosen was 25°. The method adopted consisted in shaking 200 or 300 cc. of the solution of the mixed carbonates, contained in a closed liter bottle, with air until equilibrium was reached, the whole being kept at constant temperature. A sample of the gas was transferred to another vessel and its percentage of carbon dioxide determined. The composition of the solution was determined by analysis.

A number of the best methods of analyzing carbonate solutions have been critically studied by Küster.[2] The result of this careful piece of work was to show that, of all methods, that of Winkler is most accurate. This method, as applied to solutions containing bicarbonates, consists in adding, in ex-

[1] J. Phys. Chem., **5**, 537 (1901).
[2] Ztschr. anorg. Chem., **13**, 127 (1897).

cess, a known volume of standard alkali, free from carbonate, precipitating the carbonate by addition of barium chloride, and finally titrating the excess of alkali with hydrochloric acid, using phenolphthaleïn as indicator.

This method was tested by means of preliminary analyses, carried out as follows : The necessary amount of barium chloride solution was first brought into an 80 cc. flask, then the measured volume of standard alkali was added, and finally 10 cc. of the carbonate solution was run into this directly from the pipette. When two or three analyses of the same solution were to be made, the flasks were all charged with the barium chloride and standard alkali, and corked. Then the carbonate solution was measured from the pipette into each flask with as little loss of time as possible. After mixing, the flasks were tightly closed with rubber stoppers and allowed to stand a few minutes, after which the excess of alkali was titrated with decinormal hydrochloric acid. The net amount of alkali used (that is, the whole amount added less that neutralized by acid in the final titration) is a measure of the carbon dioxide in excess of that existing as normal carbonate.

In three determinations, using in each 9.90 cc. of a bicarbonate solution, there were required, in each analysis, exactly 10.60 cc. of the standard barium hydroxide solution. In three other determinations, using in each 9.90 cc. of a different bicarbonate solution, there were required 10.42, 10.42, and 10.40 cc., respectively, of barium hydroxide. By working in the manner just described, no carbon dioxide could be lost by the bicarbonate solution in the course of the analysis, and practically none absorbed from the air by the standard alkali.

Carbon dioxide may readily be lost during analysis from solutions rich in bicarbonate, if care be not taken to render them alkaline at once. Low results were invariably obtained when, instead of working in the manner described, the bicarbonate solutions were measured into beakers and allowed to stand, even for four or five minutes, before adding an excess of alkali.

The concordant results given above, together with those of the elaborate work of Küster, are sufficient to show the accuracy of the analytical method used in the determination of the carbon dioxide in the solutions.

In order to calculate the amounts of carbonate and bicarbonate in any solution containing a known amount of carbon dioxide, it is necessary to know the total amount of sodium. This was determined by titration with standard hydrochloric acid, using methyl orange as indicator, and taking for the end reaction the "normal color" produced by the indicator when dissolved in water saturated with carbon dioxide. This method, recommended by Küster,[1] gives excellent results.

For the determination of carbon dioxide in mixtures of this gas with air, the sample was brought into a half-liter separatory-funnel closed by a perforated stopper. An excess of barium hydroxide was run in rapidly from a burette by inserting the tip of the burette in place of the glass plug of the rubber stopper. A solid stopper was then substituted for the perforated one. In doing this a quantity of gas escaped equal in volume to that of the barium hydroxide added. The solution was shaken vigorously with the gas for ten minutes. (Absorption of the carbon dioxide seemed to be complete in from one to two minutes.) The excess of alkali was then determined by titration with standard hydrochloric acid. Phenolphthaleïn was used as indicator.

The transference of the gas from the equilibrium-bottle to the vessel in which it was analyzed required some care. For, since the equilibrium depends on the temperature and pressure, any change in these conditions during the process of separation of the phases is not permissible. The equilibrium-vessel consisted of a liter bottle. It was fitted with a rubber stopper, through one hole of which passed the stem of a 100 cc. separatory-funnel, through the other hole a bent tube with glass stop-cock. The stem of the separatory-funnel nearly reached the bottom of the bottle. The carbonate solution, to the amount of 200 to 300 cc., was placed in the bottle and the stopper, carrying the separatory-funnel and tube,

[1] *Loc. cit.*

was inserted and carefully wired.   The bottles thus charged
were placed in a large thermostat, the temperature of which
was kept constant at 25° (±0.01°).   While in the thermostat,
the bottles were constantly shaken by means of a device giv-
ing a rather rapid rocking motion.   The total pressure of the
gas phase was made nearly equal to the normal atmospheric
pressure by opening the stop-cock of the bent tube occasion-
ally during the first hour or two after starting.   The attain-
ment of equilibrium under these conditions required two or
three days, as shown by special experiments made to deter-
mine this point.   In the recorded experiments the time al-
lowed was five days or more.   Immediately before removing
a bottle from the thermostat, preparatory to the analysis of
its contents, the gas pressure was determined by measuring,
with a simple manometer, the excess or deficiency of pressure
with respect to the existing barometric pressure.   This was
readily done by attaching the manometer to the bent tube
having the stop-cock.   The transference, for analysis, of the
larger part of the gas to a large separatory-funnel of known
volume was accomplished at constant (atmospheric) pressure
in the following manner :   The end of the bent tube of the
equilibrium apparatus was connected by a short rubber tube
with one tube of a three-way stop-cock.   A second tube of
the three-way cock was connected by a rubber tube with a
perforated rubber stopper which fitted the large funnel, into
which the gas was to be transferred.   The third tube of the
three-way cock was attached to a thin-walled rubber bulb of
about 50 cc. capacity.   To transfer the gas, the stem of the
small separatory-funnel of the equilibrium apparatus was
filled with the carbonate solution by applying suction at the
mouth of the funnel and opening its stop-cock, the other cock
of the apparatus being meanwhile kept closed.   The small
separatory-funnel was then filled with pure dry mercury, and
the rubber bulb and the tubes leading to the large funnel
were rinsed with the gas which was displaced by allowing the
mercury to run into the equilibrium-bottle. The large separa-
tory-funnel was completely filled with mercury and connected
with the delivery-tube from the three-way cock.   It was sup-

ported above the equilibrium-bottle in such a way that the mercury could flow from the former into the smaller separatory-funnel. By opening the stop-cocks of the two separatory-funnels partially and the other two cocks completely, the gas was readily transferred. The rubber bulb, being in direct communication with the two vessels, indicated, by its dilations or contractions, the adjustments necessary to secure an equal flow of mercury through the two stop-cocks. It served, at the same time, to keep the pressure equal to the barometric pressure. Constant temperature, during transference, was secured by placing the bottle in a vessel of water kept at 25° (±1°).

The main series of experiments was made with solutions of bicarbonate and carbonate in various proportions, and of decinormal strength with respect to sodium. Such solutions, of approximately the desired composition, were made from separate solutions of bicarbonate and carbonate, each having the same concentration of sodium.

The method of calculating the equilibrium constant from the analytical data can doubtless best be shown by an example (Experiment 1, Table II.).

Analysis of the Gas.

Volume of the separatory-funnel	550 cc.
Barometric pressure	743 mm.
Excess pressure in equilibrium-bottle	2 "
Total " " "	745 "
Temperature of the gas in the separatory-funnel immediately before analysis	28.2°

Added 10 cc. dilute barium hydroxide (= 2.15 cc. N/10 hydrochloric acid). Ten cc. of gas escaped. After absorption of the carbon dioxide, the excess of alkali required, using phenolphthaleïn, 1.44 cc. of acid.[1]

2.15 — 1.44 = 0.71 cc. N/10 acid.

1 cc. of N/10 acid = 1.12 cc. of carbon dioxide gas at 0° and 760 mm.

---

[1] In titrations requiring small volumes of solutions (as in this case) a special gravimetric burette, holding about 4 cc., was employed, and the amounts of solution used were determined by weighing. Much greater accuracy was thereby secured.

0.71 × 1.12 = 0.79 cc = the volume of the carbon dioxide at 0° and 760 mm.

$$\frac{0.79 \times (273 + 28) \times 760}{540 \times 273 \times 743} =$$ the fraction of the total pressure exerted by the carbon dioxide.

The total pressure of the vapor phase is $\frac{745}{760}$ of one atmosphere.

Therefore, the partial pressure of the carbon dioxide, P, is

$$\frac{0.79 \times 301 \times 745}{540 \times 273 \times 743} = 0.00161 \text{ atmosphere.}$$

From which we get :

$$k\,P = 0.0338 \times 0.00161 = C_4.$$

Analysis of the Carbonate Solution.

The exact concentration of the carbonate solution was found from the titration in presence of methyl orange :

9.94 cc. of carbonate solution required 9.93 cc. of N/10 acid.

Therefore the solution was 0.0999 normal with respect to sodium.

9.94 cc. of the carbonate solution was run into 7.49 cc. N/10 barium hydroxide and 2 cc. of approximately N/2 barium chloride. The excess of alkali required 0.70 cc. N/10 hydrochloric acid. The difference, 6.79 cc., was, therefore, the amount of barium hydroxide required to neutralize all of the carbon dioxide in the solution in excess of that needed to form the normal carbonate with the sodium. The larger part of this was united to form bicarbonate, but a small amount was present as free carbonic acid. The concentration of the free carbonic acid, considered as monobasic, has just been found to be 0.00161 × 0.0338 normal. In neutralizing barium hydroxide it is dibasic. The volume of N/10 barium hydroxide required to neutralize 10 cc. of carbonic acid of this strength is, therefore :

10 × 10 × 2 × 0.0161 × 0.0338 cc. = 0.01 cc., the correction for the free carbonic acid in the solution.

$6.79 - 0.01 = 6.78$ cc., the amount of barium hydroxide required for the bicarbonate alone.

$$6.78/9.93 = 0.683.$$

68.3 per cent of the sodium was in the form of bicarbonate. The duplicate analysis gave 68.1 per cent. Mean, 68.2 per cent. Therefore,

$x = 0.682.$ $1 - x = 0.318.$ $P = 0.00161,$ $k = 0.0338.$

Substituting these values in the formula

$$\frac{2x^2 \, C}{kP(1-x)} = K,$$

we get

$$\frac{2 \times 0.682^2 \times 0.0999}{0.0338 \times 0.00161 \times 0.318} = 5320 = K.$$

The following table shows the results obtained with solutions decinormal with respect to sodium. The fourth column contains the apparent percentages, A, of bicarbonate. These values, corrected in the manner described for the free carbonic acid in the solution, give the real percentages of bicarbonate as contained in the fifth column :

Table II.

	Barometric pressure.	Excess pressure.	A.	100x.	100P.	K × 10⁻².
1	743	2	68.3	68.2	0.161	53.2
2	740	2	69.1	69.0	0.159	57.0
3	745	2	76.2	76.0	0.259	54.6
4	742	3	77.7	77.5	0.294	53.6
5	743	10	78.3	78.1	0.322	51.0
6	743	3	82.1	81.8	0.404	53.6
7	745	0	96.6	95.1	2.23	49.0
8	740	24	103.6	98.5	7.49	51.0
					Mean,	52.9

The above results represent all experiments carried to completion on solutions of this concentration, after the method, as described, had been fully worked out. An inspection of the formula for the equilibrium constant will show that, for certain proportions of the reacting substances, very small er-

rors in the analyses will cause large errors in the value of K. This is obviously the case, on the one hand, when the percentage of bicarbonate becomes so high that $1 - x$ approaches zero and, on the other hand, when P becomes very small on account of the large proportion of carbonate. The most favorable condition for the accurate determination of K is found when x lies between 75 and 85 per cent. In accordance with this it may be seen, from the table, that the smallest variations in the value of K are found between these limits. The average value of K, as given by these four determinations, is 53.2×10^2. This is the most probable value of the constant.

Walker[1] has calculated, from the ionization constant of carbonic acid, the theoretical value of the hydrolytic dissociation of sodium bicarbonate. This was done by means of the well-known formula of Arrhenius[2] which here becomes

$$K_1 = \frac{K_{H_2O}}{K_{H_2CO_3}}.$$

The closely agreeing results of the determinations of the magnitude of the dissociation constant of water by Ostwald,[3] Wys,[4] Arrhenius,[5] and Kohlrausch and Heydweiller,[6] give as an average value,[7]

$$K_{H_2O} = 1.2 \times 10^{-14}.$$

The constant of carbonic acid, as measured by the conductivity method by Walker and Cormack,[8] gave the value,

$$K_{H_2CO_3} = 3.04 \times 10^{-7},$$

the concentration of the carbonic acid being expressed in gram-molecules per liter.

Therefore,

$$K_1 = \frac{1.2 \times 10^{-14}}{3.04 \times 10^{-7}} = 3.95 \times 10^{-8}.$$

[1] Ztschr. phys. Chem., **32**, 137 (1900).
[2] *Ibid.*, **5**, 17 (1890).
[3] *Ibid.*, **11**, 521 (1893).
[4] *Ibid.*, **11**, 492 (1893).
[5] *Ibid.*, **11**, 827 (1893).
[6] *Ibid.*, **14**, 317 (1894).
[7] Van 't Hoff : Vorlesungen, **1**, 127.
[8] J. Chem. Soc. (London), **77**, 5 (1900).

But

$$K_1 = \frac{C_{NaOH} \times C_{H_2CO_3}}{C_{NaHCO_3}}. \qquad \text{(Equation 1.)}$$

From these relationships Walker obtained the hydrolytic dissociation of a decinormal solution of sodium bicarbonate, 0.06 per cent. This value is really fictitious, for the reason shown on page 440. This is clearly seen when we consider that for 0.06 per cent hydrolysis the concentration of the carbonic acid in the decinormal bicarbonate solution would be 0.00006 normal molecular. The concentration of carbonic acid in water, saturated at atmospheric pressure at 25°, is 0.0338 normal molecular. Therefore, the pressure of a 0.00006 normal solution is only 0.0018 atmosphere. From Table II. it is seen that a decinormal solution containing but 96 per cent of bicarbonate gives a partial pressure of more than twelve times this amount.

The actual concentrations of the free carbonic acid and of the sodium hydroxide in a decinormal solution, made from solid bicarbonate and water in such a way that no carbon dioxide is allowed to escape, may readily be calculated. Since the amount of free hydroxide in such a solution is extremely minute, as is shown below, we may represent the net result of the hydrolytic dissociations thus:

$$2NaHCO_3 \; \rightleftarrows \; Na_2CO_3 + H_2CO_3.$$
$$C_1 C_2 C_4$$
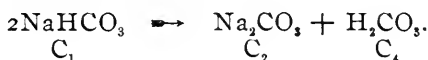
If

$$\frac{x}{V} = C_1. \qquad \frac{1-x}{2V} = C_2 = C_4.$$

$$K = \frac{C_1^2}{C_2 C_4} = \frac{4x^2}{(1-x)^2} = 5290.$$

From which

$$x = 0.9732 \qquad \text{and} \qquad 1 - x = 0.0268.$$

In such a solution 2.68 per cent of the bicarbonate would have been converted into carbonate and free carbonic acid. It will be observed, further, that the equation involving x does not contain V. The value of x is, therefore, independent of the dilution. For a decinormal solution

$$C_4 = \frac{1 - x}{2 \times 10} = 0.00134;$$

$$P = \frac{0.00134}{0.0338} = 0.0396;$$

from which it follows that a decinormal solution of sodium bicarbonate will evolve carbon dioxide if the partial pressure of the gas is less than 4 per cent of 1 atmosphere. Now for the bicarbonate solution we have

$$K_1 = \frac{C_{NaOH} \times C_{H_2CO_3}}{C_{NaHCO_3}} = 3.95 \times 10^{-8};$$
$$C_{H_2CO_3} = C_4 = 0.00134;$$
$$C_{NaHCO_3} = C_1 = 0.097.$$

Therefore,

$$C_{NaOH} = 2.9 \times 10^{-6}.$$

This value, which is but 1/20 of that calculated by Walker,[1] represents the true degree of alkalinity of a freshly prepared decinormal solution of sodium bicarbonate. Solutions consisting of mixtures of bicarbonate and carbonate contain, of course, more free sodium hydroxide. Thus the concentration of sodium hydroxide in solution 1, Table II., is readily calculated to be 5.0×10^{-5}.

According to equation 3, page 441, we have

$$K_2 = KK_1,$$

where K_1 is the constant for the hydrolytic dissociation of sodium bicarbonate and K_2 that for the carbonate,

$$K = 5290; \qquad\qquad K_1 = 3.95 \times 10^{-8};$$

from which

$$K_2 = 2.08 \times 10^{-4}.$$

The percentage of hydrolytic dissociation of sodium carbonate may be calculated from the value of this constant by means of the formula,

$$K_2 = \frac{m^2}{(1 - m)V} = 2.08 \times 10^{-4},$$

[1] Ztschr. phys. Chem., **32**, 137 (1900).

where m is the fraction of the carbonate existing as hydroxide and bicarbonate. For a solution containing 0.5 gram-molecule in 10 liters, $m = 0.062$. That is, in a solution decinormal with respect to sodium, 6.2 per cent of the sodium carbonate is split by the action of water into sodium hydroxide and sodium bicarbonate. The concentration of the hydroxide in such a solution is 0.0031 normal.

The hydrolytic dissociation of sodium carbonate has been studied by Shields.[1] The amount of free base was calculated from the velocity of saponification of ethyl acetate at $24°.2$. Shields gives as the value of the constant for a 0.0477 gram-molecular solution[2]

$$(100)K_2 = 0.02382.$$

That is,

$$K_2 = 2.38 \times 10^{-4},$$

while I find, at $25°$,

$$K_2 = 2.08 \times 10^{-4}.$$

The agreement seems to be very good. But it appears, upon critical inspection of the method of calculation, that Shields has assumed that each molecule of carbonate, when hydrolyzed, gives 2 molecules of hydroxide, thus :

$$Na_2CO_3 + 2H_2O \;\longrightarrow\; 2NaOH + H_2CO_3.$$

As this is not the case to any appreciable extent, it would seem that the method of calculation is not correct. The results of these experiments of Shields have been recalculated for the 0.0477 molecular solution on the basis of a dissociation into 1 molecule each of hydroxide and bicarbonate. The average value of K_2 thus found is 1.04×10^{-4}, from which the percentage of carbonate molecules changed to hydroxide and bicarbonate is calculated to be 4.6. My own experiments lead to the value 6.2 per cent for a 0.05 gram-molecular solution. Shields calculates that 4.87 per cent of the carbonate molecules each give two of hydroxide.

[1] Ztschr. phys. Chem., **12**, 167 (1893).

[2] Shields calls this K and not 100K, as I have written it and as it really should be. See van Laar : *Ibid.*, **12**, 745 (1893).

Walker and Cormack[1] have shown that the ionization of carbonic acid is chiefly into H and HCO_3. The constant for the second H ion is fixed by the relation,

$$C_H \times C_{CO_3} = K_3 C_{HCO_3}.$$

The value of K_3 has been calculated by Bodländer[2] from the work of Shields. Bodländer finds

$$K_3 = 1.295 \times 10^{-11}.$$

K_3 may be calculated from any experiment recorded in Table II. Experiment 6 may be chosen, as it probably represents the most favorable composition for the accurate analytical determination of all the factors, x, $1 - x$, and P.

$$x = 0.818. \qquad 1 - x = 0.182. \qquad P = 0.00404.$$

Since practically all of the HCO_3 ions come from the sodium bicarbonate, we have

$$C_{HCO_3} = 0.1 \times 0.818 \times \alpha,$$

where α is the degree of ionization of the bicarbonate. By an extrapolation of Walker and Cormack's figures the degree of ionization of 0.1 molecular sodium bicarbonate is calculated to be 0.81. Therefore,

$$C_{HCO_3} = 0.0818 \times 0.81 = 6.63 \times 10^{-2}.$$

Similarly the concentration of CO_3 depends upon the concentration of the sodium carbonate and on its degree of ionization. If we consider the ionization of the carbonate to be the same as that of sodium sulphate,[3] at equal concentration, we have for a 0.05 molecular solution 0.70. Therefore,

$$C_{CO_3} = 0.5 \times 0.0182 \times 0.70 = 6.37 \times 10^{-3}.$$

Now,

$$C_H \times C_{HCO_3} = 3.04 \times 10^{-7} \times C_{H_2CO_3};$$

$$C_{H_2CO_3} = 0.00404 \times 0.0338 = 1.37 \times 10^{-4};$$

$$C_H = \frac{3.04 \times 1.37 \times 10^{-11}}{6.63 \times 10^{-2}} = 6.28 \times 10^{-10}.$$

[1] J. Chem. Soc. (London). **77**, 5 (1900).

[2] *Loc. cit.*

[3] Kohlrausch: Wied. Ann., **26**, 161 (1885).

Therefore,

$$K_3 = \frac{6.28 \times 6.37 \times 10^{-13}}{6.63 \times 10^{-2}} = 6.04 \times 10^{-11}.$$

The considerable difference between this result and that of Bodländer is in large measure due to Shields' error in calculating the hydrolysis of sodium carbonate. A comparison of K_3 with the ionization constant for the first H ion of carbonic acid shows that the latter is 5040 times as large as the former. Since the degrees of ionization, at the same concentration, of two weak acids are proportional to the square roots of their ionization constants, the degree of ionization of the first H ion of carbonic acid is $\sqrt{5040}$, or 71 times as great as that of the second H ion. The ionization constants of several very weak acids are all greater than K_3, as the following figures of Walker and Cormack show :

	Constant $\times 10^{-10}$.
Carbonic acid (first H ion)	3040.0
Hydrogen sulphide	570.0
Boric acid	17.0
Prussic acid	13.0
Phenol	1.3
I find : Carbonic acid (second H ion) $= K_3$	0.6

In very dilute solutions sodium bicarbonate is highly ionized into Na and HCO_3. The ionization, K_4, of sodium bicarbonate as an acid is, therefore, practically equal to K_3 for such solutions. Sodium bicarbonate may also split into H and $NaCO_3$ ions, and it is probable that the constant of this ionization is about the same as K_3. If this is the case, K_4 in solutions not dilute is also nearly equal to K_3. The constant, K_4, may also be obtained, at least approximately, by dividing the constant for the dissociation of water by K_2, the constant for the hydrolytic dissociation of sodium carbonate.

$$K_4 = \frac{K_{H_2O}}{K_2} = \frac{1.2 \times 10^{-14}}{2.08 \times 10^{-4}} = 0.58 \times 10^{-10},$$

a quantity which does not differ greatly from the value of K_3 found above.

The formula for the equilibrium of the system composed of

carbon dioxide and the aqueous solution of the carbonates of sodium, has been derived upon the supposition that the solution was dilute. It is not to be expected, therefore, that the value of K would be the same for concentrated solutions. Deviations from the simple relationships, which hold for dilute solutions, may be due to three causes : (1) The partial failure of the law of mass action ; (2) the change in the ratio of the degrees of ionization, as salts, of the two carbonates ; (3) a smaller solubility of carbon dioxide in the stronger solutions than in the dilute solutions, where the solubility has been assumed to be the same as in pure water. Equilibrium experiments with 0.3 normal (Table III.) and with normal solutions (Table IV.) actually gave lower values for K than were found for decinormal solutions, but there is good agreement between various determinations at the same concentration. The following tables show the results obtained :

Table III.

	Barometric pressure.	Excess pressure.	A.	$100x$.	$100P$.	$K \times 10^{-2}$.
1	747	0	58.0	57.9	0.319	44.6
2	748	0	68.0	67.9	0.583	43.8
3	745	0	77.1	76.9	1.044	43.6
4	740	3	85.6	85.2	1.07	44.4
5	740	3	89.4	88.8	2.76	45.4
6	743	2	93.6	92.6	4.51	45.8

Mean, 44.6

Table IV.

	Barometric pressure.	Excess pressure.	A.	$100x$.	$100P$.	$K \times 10^{-2}$.
1	744	0	76.1	75.8	4.36	32.4
2	737	6	81.4	81.0	6.24	32.8
3	742	2	86.7	86.0	10.21	30.6
4	743	1	91.3	90.2	16.82	29.2

Mean, 31.2

Equilibrium in Carbonate-bicarbonate Solutions in Contact with Natural Air.

The determination of the amount of carbon dioxide in the air has been the subject of a very large number of extended

researches. In a recent paper[1] Letts and Blake have given the results of their own very careful experiments, made at Belfast, together with a tabulated summary of several thousand analyses, made by many observers, in various parts of the world. This summary clearly shows that the percentage of carbon dioxide in air (collected out of doors) is by no means constant. But, if analyses of air from the central portions of crowded cities be excluded, all except a small portion of the results fall between the limits of 2.5 and 3.5 parts by volume of carbon dioxide in 10,000 of dry air. The average value is probably not far from 3 parts in 10,000.

Taking the amount of carbon dioxide as fixed at this value, we may calculate the theoretical composition of carbonate-bicarbonate solutions when in equilibrium with ordinary air, at a temperature of 25°. In the formula

$$\frac{2x^2\,C}{kP(1-x)} = K.$$

P, the partial pressure of the carbon dioxide, is equal to

$$\frac{0.0003H}{760},$$

where H is the barometric pressure (corrected for aqueous tension) at the time of the experiment. Transposing, we have

$$\frac{x^2}{1-x} = \frac{K \times H \times 0.0338 \times 0.0003}{2 \times 760 \times C}. \tag{4}$$

In the work of Cameron and Briggs, which has been previously mentioned, one series of experiments on the carbonates of sodium was carried out at 25°. The theoretical results, as indicated by the above formula, have been calculated and compared with the values obtained by these chemists. In making the calculation, H, the corrected barometric pressure, has been assumed equal to 730 mm. The value of K for dilute solutions is practically 53×10^{-2}. The values of K used in calculating the theoretical values of x, for the more concentrated solutions, were obtained by interpolation from the average values of K as found in Tables III. and IV.

---

[1] Proc. Roy. Soc. (Dublin), (1900), pp. 107-279.

The comparison of Cameron and Briggs's results with the theoretical values is shown in the following table :

Table V.

Concentration of sodium in gram-atoms per liter.	Value of $K \times 10^{-2}$, used.	Percentage, x, of sodium existing as bicarbonate.	
		Found by C. and B.	Calculated.
0.0044	53	91.3	87
0.0143	53	80.0	72
0.0562	53	62.7	49
0.2248	48	40.7	28
0.8847	33	36.0	13

The differences between the calculated results and those actually found by Cameron and Briggs were so great, especially for the more concentrated solutions, that I was led to make a few experiments of the same nature.

The results of a preliminary experiment may serve to show in a roughly quantitative way the rate of change of composition of an approximately decinormal solution of sodium bicarbonate when a stream of air (taken from out of doors) is drawn through it at the ordinary temperature of the laboratory.

Table VI.

Time in hours.	Percentage of sodium existing as bicarbonate.
0	95
0.25	88
0.67	80
1.17	76
2.00	75
26.0	45
32.0	44
48.0	43
72.0	40
144.0	40

A state of equilibrium is, therefore, reached after about three days.

In a second similar experiment, air was drawn through a solution of sodium carbonate having the same concentration of sodium as the preceding bicarbonate solution. The result was as follows :

Table VII.

Time in hours.	Percentage of sodium existing as bicarbonate.
0	0.3
5.5	5.0
17.0	17.0
24.0	26.0
70.0	40.0

The same state of equilibrium is reached, of course, whether one starts with a carbonate or a bicarbonate solution.

In the following experiments about 200 cc. of the bicarbonate solution were placed in a large Drechsel wash-bottle, which was immersed in a thermostat kept at $25°$ ($\pm 0.01°$). The bottle containing the bicarbonate solution was connected on the one side with an aspirating pump and on the other with a wash-bottle containing pure water. Pure air (from out of doors) was supplied by a tube connected with the wash-bottle.

The pressure in the bottle containing the bicarbonate solution was measured by means of a manometer. It was always 8 to 10 mm. (of mercury) less than the atmospheric pressure. The corrected pressure, as given in Tables VIII., IX., and X., is the barometric pressure, corrected for aqueous tension and for the diminution just mentioned.

The following results were obtained in this way, starting with a decinormal solution of sodium bicarbonate.

Table VIII.

Time in days.	Concentration of sodium in gram-atoms per liter.	Corrected pressure.	Percentage of sodium existing as bicarbonate. Found.	Calculated.
0	0.100		95.0	$(K = 53 \times 10_2)$
2			44.1	
3	0.101	710	40.6	39.0
3.2	0.101	713	40.8	39.0

The figures in the last column were obtained by means of Equation 4, page 457, K being taken as 53×10^2. The fact that the solution slowly became slightly more concentrated shows that the air entering the solution was not completely saturated with water vapor.

The results with more concentrated solutions are given in Tables IX. and X.

Table IX.

Time in days.	Concentration of sodium in gram-atoms per liter.	Corrected pressure.	Percentage of sodium existing as bicarbonate.	
			Found.	Calculated.
(First series.)				
0	0.300		33.0	$(K = 45 \times 10^2)$
1			26.2	
2			24.8	
3	0.312	710	23.9	22.9
(Second series.)				
0	0.300		22.7	
1	0.306	711	23.1	23.2
2	0.314	714	22.5	22.9

Table X.

Time in days.	Concentration of sodium in gram-atoms per liter.	Corrected pressure.	Percentage of sodium existing as bicarbonate.	
			Found.	Calculated.
0	1.00		13.8	$(K = 31 \times 10^2)$
2	1.03	710	12.2	11.3
3	0.98[1]	714	12.9	11.5
5	0.98	715	12.9	11.5

In the second series of experiments, Table IX., the solution at the start contained a smaller amount of bicarbonate than at the end of one day. This indicates that an absorption of carbon dioxide from the air must have occurred.

A variation in the amount of carbon dioxide in the air necessarily causes a variation in the percentage of bicarbonate in a solution of given concentration. Calculation shows that an increase of 10 per cent of the total carbon dioxide in the air would cause an increase, in a decinormal solution, of only 1.4 per cent of the sodium existing as bicarbonate. In Table VIII., taking the amount of carbon dioxide in the air as 3 parts in 10,000, the percentage of bicarbonate was calculated to be 39.0. For 3.3 parts of carbon dioxide in 10,000 of air the amount would, therefore, be 40.4 per cent. The increase in bicarbonate, for a 10 per cent increase of carbon dioxide, would be 0.9 per cent for a 0.3 normal solution, and for a normal solution but 0.5 per cent.

The ordinary variations in the carbon dioxide content of air rarely exceed ±10 per cent from the assumed value, 3 parts

[1] The solution was slightly diluted at the end of the second day.

in 10,000 (except in certain localities). Such variations would consequently affect but slightly the state of equilibrium of solutions in contact with the air. In accordance with this it is seen that the agreement between the observed values and those calculated upon the basis of the average concentration of carbon dioxide in the air is very good ; and, further, that the small existing differences are no greater than may be accounted for by changes in the amount of atmospheric carbon dioxide.[1]

These experiments are, therefore, in complete accord with those of the main series. This being the case, it is difficult to understand the cause of the widely different results obtained by Cameron and Briggs. A possible source of error may be suggested. The authors do not state whether the air used was drawn from out-of-doors or was simply indoor air. In the latter case the amount of carbon dioxide may have been very much higher than in normal air. This would lead to a displacement of the equilibrium in the direction found.

Summary.

1. It has been shown experimentally that the equilibrium in the system composed of sodium carbonate, sodium bicarbonate, carbon dioxide, and water is governed, at constant temperature, by the formula

$$\frac{2x^2C}{kP(1-x)} = K,$$

in which the symbols have the following significance : x is the fraction of sodium in the form of bicarbonate ; $1-x$ is the fraction in the form of carbonate ; C is the concentration of the sodium in gram-atoms per liter ; k is the solubility coefficient of carbon dioxide in water at the equilibrium temperature ; and P is the partial pressure of the carbon dioxide. For dilute solutions $K = 53 \times 10^2$.

[1] As has been mentioned, analyses seem to show that the percentage of carbon dioxide in the air of the crowded portions of large cities is considerably higher than normal. The laboratory of the University of Chicago, where the experiments here described were made, is 6 or 7 miles distant from the central crowded parts of the city, and but a mile from Lake Michigan. In consequence the air used was probably of about normal composition.

2. The degree of hydrolytic dissociation of sodium bicarbonate, as calculated from the ionization constant of carbonic acid, is rendered fictitious by the fact that the bicarbonate is itself a weak acid. The acid carbonate reacts with the free hydroxide produced by the primary hydrolysis, and, on account of its relatively great concentration as compared with that of the free carbonic acid, greatly displaces the equilibrium that would be expected to result from the first action of water on the bicarbonate. For a decinormal solution, the free hydroxide is thereby reduced to about 1/20 of the amount calculated by Walker.

3. The degree of hydrolytic dissociation of sodium carbonate was calculated from the equilibrium experiments. In a solution containing 0.5 gram-molecule of sodium carbonate in 10 liters, 6.2 per cent of the carbonate exists as hydroxide and bicarbonate.

4. The ionization constant of sodium bicarbonate, as an acid, is nearly equal to the constant of the second H ion of carbonic acid. The latter constant is equal to 6.0×10^{-11}, which is but 1/5040 as great as that of the first H ion of carbonic acid.

5. It has long been known that bicarbonate solutions lose carbon dioxide in contact with the air, giving a mixture of carbonate and bicarbonate. The state of equilibrium reached depends on the concentration of the solution, and may be calculated by means of the equilibrium formula, by considering the amount of carbon dioxide in the air as known.

6. The formula given above will hold equally well for solutions of the carbonates of any highly ionized monacid bases. It is probable that it may also be applied to salts of such acids as hydrogen sulphide and sulphurous acid.

Work is being continued along these lines in this laboratory by Mr. H. G. Knight.

THE EXISTENCE OF HYDROGEN TETROXIDE.

By A. M. Clover.

Hydrogen dioxide, in aqueous solution, behaves as a weak acid. Hanriot[1] and Wolffenstein[2] have proved that a solution of the pure substance reddens litmus. Schönbein,[3] in 1859, noted that hydrogen dioxide could be extracted from an ethereal solution to a much greater extent by a solution of alkali than by pure water. This fact makes it quite probable that hydrogen dioxide enters into chemical union with the alkali.

Calvert[4] has recently studied the condition of hydrogen dioxide in alkaline solution, and in several ways has succeeded in proving that this substance neutralizes alkalies by entering into chemical union with them.

The fact is well known that solutions of the hydroxides of the alkaline-earth metals are precipitated by hydrogen dioxide with the formation of hydrated peroxides of the type $BaO_2.8H_2O$. On the other hand, these substances are dissolved by acids with the liberation of the corresponding amount of hydrogen dioxide. They are therefore to be looked upon as the salts of hydrogen dioxide.

Sodium dioxide,[5] Na_2O_2, is formed when sodium is oxidized in air. The hydrated compound, $Na_2O_2.8H_2O$,[6] separates in the crystalline state, on concentrating a solution of hydrogen dioxide containing the calculated amount of sodium hydroxide. Both of these last-named compounds dissolve in dilute acids with the liberation of the corresponding amount of hydrogen dioxide, and are also to be considered as the salts of this substance. Compounds of potassium[7] and lithium[8] similar to those already mentioned have been studied.

When potassium or rubidium is oxidized by means of air or

[1] Compt. rend., **100**, 172 (1885).

[2] Ber. d. chem. Ges., **27**, 3311.

[3] J. prakt. Chem., [1], **78**, 92.

[4] Ztschr. phys. Chem., **38**, 513.

[5] Harcourt: J. Chem. Soc. (Qu. J.), **14**, 267.

[6] Schöne : Ann. Chem. (Liebig), **193**, 241.

[7] Erdmann and Köthner : *Ibid.*, **294**, 55.

[8] *Loc. cit.*

oxygen, the compounds formed have a percentage composition represented by the formulas KO_2 and RbO_2. Nothing is known concerning the molecular weight of these substances and it is possible that their molecules are represented by the formulas K_2O_4 and Rb_2O_4, just as the peroxide of sodium is ordinarily represented by the formula Na_2O_2, on account of its relation to hydrogen dioxide, whose formula, H_2O_2, has been demonstrated by molecular weight determinations.[1] In this light the peroxides of potassium and rubidium are to be considered as derivatives of the hypothetical tetroxide of hydrogen, H_2O_4.

This view has led Bach[2] to examine the solution obtained by dissolving potassium tetroxide in dilute acid, for the presence of some oxide of hydrogen other than the dioxide. The results of his experiments have led him to conclude that the solution mentioned contains a considerable amount of a higher peroxide which he assumes to be hydrogen tetroxide, H_2O_4.

Wishing to further examine the properties of so interesting a substance, I have attempted to prepare it according to the method of Bach. However, the solution which I have obtained has behaved in all respects as a solution of hydrogen dioxide, and I have not been able, in any way, to detect the presence of any other substance. I have been led, therefore, to repeat the work of Bach with much care, and am forced to conclude that his experimental work is in error, and that there is no evidence whatever of the existence of hydrogen tetroxide.

In examining the solution supposed to contain higher oxides of hydrogen, Bach has made use of the well-known reaction between hydrogen dioxide and potassium permanganate, which takes place according to the following equation:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 =$$
$$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$
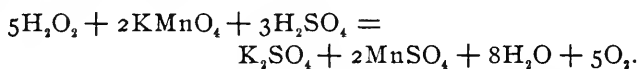
The reaction takes place quantitatively, and the amount of hydrogen dioxide in a solution may be estimated by noting the amount of permanganate used or the amount of oxygen evolved.

[1] Orndorff and White : Ztschr. phys. Chem., **12**, 63.
[2] Ber. d. chem. Ges., **33**, 1506, 3111.

On treating the solution in question with permanganate, Bach has found that the amount of oxygen evolved is in large excess of the theoretical quantity. In one series of experiments the excess amounted to an average of 25 per cent. In another the average excess was 34 per cent. The calculated amount of oxygen was based upon the amount of permanganate used. Since the solution in question could contain nothing but oxides of hydrogen, together with the potassium sulphate formed in the neutralization, Bach seems perfectly justified in drawing the conclusions which he does.

The work of Bach has been previously criticized by Armstrong,[1] who, without submitting experimental evidence, has offered to explain Bach's results by assuming the formation of Caro's acid by the interaction of hydrogen dioxide with the free sulphuric acid present in the solution. This criticism is unjustified, however, in view of Bach's own work, and also in view of the experiments given below with pure hydrogen dioxide. Furthermore, it will be seen later that Bach's results are probably to be attributed to the use of insufficient acid rather than too much.

A few experiments are here given to show what influence the amount of acid used has on the reaction between hydrogen dioxide and permanganate.

I. 5 cc. of a solution of pure hydrogen dioxide[2] were added to a large excess of dilute sulphuric acid (normal) and titrated with $N/10$ permanganate.

	Required. cc.
1	12.8
2	12.8

II. 5 cc. of the same solution were added to a solution of potassium iodide in dilute sulphuric acid and the iodine liberated was estimated by means of $N/10$ thiosulphate.

	Required. cc.
1	12.7
2	12.75

[1] Proc. Chem. Soc., **16**, 134.
[2] Jones, Barnes, and Hyde : This JOURNAL, **27**, 22.

III. 5 cc. of the same solution were then added to 7.8 cc. N/10 sulphuric acid (calculated amount 7.7 cc.) and titrated with N/10 permanganate.

	Required. cc.
1	12.8
2	12.7

To obtain these results, however, it was necessary to add the permanganate very slowly toward the last, otherwise a considerable quantity of manganese dioxide was precipitated which redissolved very slowly. The results then obtained were low.

IV. 5 cc. of the same solution were added to 3.9 cc. N/10 sulphuric acid (0.5 calculated amount). After the addition of 6.6 cc. N/10 permanganate, a permanent precipitate of manganese dioxide appeared, and the solution, after standing for a few minutes, had lost practically all of the remaining hydrogen dioxide, owing to the catalytic action of the precipitate.

It will be seen from these experiments that the reaction between hydrogen dioxide and permanganate does not take place according to the equation given, unless the required amount of acid be present, and that a large excess of acid has no influence upon the reaction. The reliability of the reaction, either with the minimum quantity or with excess of acid, is shown by the estimation by means of potassium iodide and thiosulphate. I have also made certain that the presence of sodium or potassium sulphates has no influence on the reaction in question, as these substances are present in the solutions to be examined later.

The oxygen evolved by the action of permanganate upon a solution of hydrogen dioxide was also measured, in order to test the reliability of the results with the solutions of sodium dioxide and potassium tetroxide. The apparatus used was essentially that used by Bach. The reaction-flask was kept in a bath of ice-water at 0°. It was fitted with a two-hole rubber stopper, through which passed the burette containing permanganate and a capillary tube connected with a gas-

burette. The gas evolved was measured at room temperature and the proper corrections then applied. The permanganate was allowed to drop slowly into the solution, so that there was no rise in temperature.

I. 2 cc. of a solution of commercial hydrogen dioxide were added to 0.6 cc. normal sulphuric acid (calculated amount 0.53 cc., the amount of free acid in the solution having been found to be inconsiderable) and treated with permanganate as just described. At the end of the reaction the flask was shaken until the gas volume became constant.

	cc.
Oxygen evolved (corrected)	9.53
N/10 KMnO$_4$ used	8.8
Oxygen calculated from KMnO$_4$	9.85

II. The previous experiment was repeated except that 3 cc. normal sulphuric acid were used.

	cc.
Oxygen evolved (corrected)	9.54
N/10 KMnO$_4$ used	8.75
Oxygen calculated from KMnO$_4$	9.79

III. 2 cc. pure distilled hydrogen dioxide solution were added to 3.2 cc. of N/5 sulphuric acid (calculated amount 3.02 cc.) and treated as before.

	cc.
Oxygen evolved (corrected)	10.9
N/10 KMnO$_4$ used	10.1
Oxygen calculated from KMnO$_4$	11.3

It will be seen that in all cases the oxygen evolved is from 0.3 to 0.4 cc. lower than the calculated amount. This deficiency is just accounted for by the solubility of oxygen in the solution.

Potassium Tetroxide.

Bach prepared his potassium tetroxide by heating metallic potassium in a silver boat placed in a combustion-tube and heated first in a current of dry air, and finally in oxygen. The product was an orange-yellow, crystalline mass. No further details are given concerning the preparation of the

substance, nor was an analysis made.   He states that the prod-
uct was mixed with particles of black silver, which are ob-
jectionable on account of their catalytic influence upon the
solution.

I attempted to prepare the tetroxide in a flask of hard glass
heated in an air-bath at 250°, a current of dry air being passed
through the flask.   During the oxidation the product spread
itself over the entire surface of the flask and consisted of a
thin cake, difficult to remove.   I have had much better suc-
cess by using a boat of aluminium, as was done by Erdmann
and Köthner[1] in the preparation of the corresponding rubidium
compound.   During the process of oxidation the aluminium
was apparently unaffected and there was no trace of aluminium
in the product.   The oxidation was carried on in a long glass
tube placed in a combustion furnace.   The boat containing
the potassium was placed quickly in the tube which had been
previously swept out with a current of dry air.   It was then
heated gradually during the passage of the current of dry air.
At first the surface of the metal became coated, and this coat-
ing did not break until a temperature of 250° was reached.
At this point the molten metal spread itself over the bottom of
the boat and oxygen was rapidly absorbed.   The oxidation
was allowed to progress slowly at a temperature of 250° to
300°.   The oxidation began in the forward part of the boat,
where most of the oxide collected as a crystalline growth
about the sides of the boat.   After the oxidation had extended
the entire length of the boat, the passage of air was continued
for an hour or two longer, until the absorption of oxygen had
practically ceased (Product A).   Another sample of the
tetroxide was made in the same way except that it was finally
treated with a current of dry oxygen for several hours (Prod-
uct B).   The products were removed by allowing the boat to
slide from the combustion tube into a long test-tube which had
been swept out with a current of dry air.   The tetroxide was
easily detached from the sides of the boat by means of a glass
rod, and, after removing the boat, was pulverized with the
glass rod so as to make it homogeneous.   It was then trans-
ferred quickly to a smaller tube and preserved in a desiccator.

[1] *Loc. cit.*

Analysis of Products.—Two methods of analysis were employed :

(1) A weighed amount of the peroxide was introduced into a perfectly dry flask, a pinch of platinum black added, and the flask then connected with a two-hole rubber stopper, through which passed a burette containing dilute sulphuric acid, and a capillary tube leading to a gas-burette. A definite volume of dilute sulphuric acid was then allowed to drop into the flask, sufficient to more than neutralize the solution. The flask was then agitated until there was no further increase in the volume of the gas evolved. In this way all of the oxygen in excess of the monoxide, K_2O, was removed as gas, measured, and the proper corrections applied.

(2) A weighed amount of the peroxide was treated with water, a pinch of platinum black added, and the solution agitated for a few moments while heating on a water-bath. The hydrogen dioxide in the solution was thus removed and the alkali estimated by titrating with $N/10$ hydrochloric acid. In this way the amount of monoxide, K_2O, was obtained, the difference between this and the weight used being the amount of oxygen disengaged.

Product A.

		Per cent of disengaged oxygen.
0.0700 gram substance gave 0.02135 gram oxygen		30.5
0.0610 " " " 0.01839 " "		30.15
0.0439 " " required 6.5 cc. $N/10$ HCl		30.19
0.0563 " " " 8.3 " " "		30.49

Product B.

		Per cent of disengaged oxygen.
0.0689 gram substance required 9.85 cc. $N/10$ HCl		32.60
0.0529 " " " 7.55 " " "		32.71
0.0854 " " gave 0.0282 gram oxygen		33.02

These two methods not only serve as a check upon each other, but their agreement proves that the products consist purely of compounds of potassium and oxygen. The calculated per cent of " per" oxygen or oxygen in excess of the monoxide, K_2O, is :

                                              Per cent.
          For K$_2$O$_4$ 33.73
           "   K$_2$O$_3$ 25.34

The per cent of "per" oxygen in product (B) approaches very closely to the theoretical for the tetroxide, K$_2$O$_4$. Both products probably contain a certain amount of the lower oxides.

The assumption has, of course, been made that all oxygen in excess of the monoxide, K$_2$O, was capable of being disengaged. The agreement of the two methods of analysis shows that this is a fact.

Erdmann and Köthner[1] have expressed doubt whether the ultimate oxidation-product of potassium is represented by the formula K$_2$O$_4$, but in view of the analysis of product (B), there can be little doubt on this point. The difficulty in obtaining complete oxidation is probably because small portions of the incompletely oxidized product become covered and protected against further oxidation.

Examination of Solution of Potassium Tetroxide.

I. 0.89 gram of product (A) was dissolved in 13.5 cc. of normal sulphuric acid (calculated amount for neutralization, 13.3 cc.). The substance was added slowly to the cooled solution, the temperature of which was not allowed to rise above 0°.

(*a*) 2 cc. of this solution were added to a large excess of normal sulphuric acid, cooled to 0°, and the solution titrated with N/10 permanganate, the temperature of the solution being kept below 0°. Required, 17.6 cc.

(*b*) 2 cc. were added to an excess of normal sulphuric acid at room temperature and titrated with N/10 permanganate without cooling. Required, 17.6 cc.

(*c*) 2 cc. were added to an excess of normal sulphuric acid containing potassium iodide, the acid solution having been cooled to 0° before the addition. The iodine liberated was estimated by means of N/10 thiosulphate, the temperature of the solution not having been allowed to exceed 0°. Required, 17.7 cc.

[1] *Loc. cit.*

(*d*) 2 cc. were added to ice-water containing 5.6 cc. N/5 sulphuric acid (calculated amount, 5.3 cc) and titrated with N/10 permanganate as in (*a*). Required 17.7 cc.

(*e*) 1 cc. was added to 2.8 cc. N/5 sulphuric acid (calculated amount, 2.64 cc.) and titrated with permanganate at 0°, in the manner already described under the experiments with pure hydrogen dioxide.

	cc.
Oxygen evolved (corrected)	9.53
N/10 KMnO₄ used	8.8
Oxygen calculated from KMnO₄	9.85

(f) Experiment (*e*) was repeated.

	cc.
Oxygen evolved (corrected)	9.48
N/10 KMnO₄ used	8.8
Oxygen calculated from KMnO₄	9.85

(*g*) After the tetroxide solution had stood for one hour at 0°, 2 cc. were again titrated with permanganate as in (*b*). Required, 17.8 cc.

During this time there had been no visible evolution of oxygen from the original solution.

(*h*) 2 cc. were added to a like volume of a strong solution of potassium iodide in sulphuric acid. As the liberation of iodine progressed, not a trace of oxygen was evolved from the solution.

II. 1.027 grams of product (B) were dissolved in 15 cc. of normal sulphuric acid (calculated amount, 14.63 cc.) at 0°, as in I., with product (A). With this solution the experiments just described with the solution of product (A) were repeated with the same general results. The results alone are given, as the experiments were carried out in exactly the same way as the corresponding ones given under I.

(*a*) Required 18.7 cc. N/10 KMnO₄.
(*b*)   "   18.8 "   "   "
(*c*)   "   18.6 "   "   thiosulphate.
(*d*)   "   18.7 "   "   KMnO₄ (11.5 cc. N/10 H₂SO₄ used).

(*e*) 1 cc. of solution added to 2.9 cc. N/5 H$_2$SO$_4$ (calculated amount, 2.8 cc.). Required, 9.4 cc. N/10 KMnO$_4$.

	cc.
Oxygen found (corrected)	10.15
Oxygen calculated from KMnO$_4$	10.52

It is evident that the amount of oxygen evolved from this solution by treatment with permanganate bears the same relation to the amount of permanganate used as with the solution of pure hydrogen dioxide. In these experiments the minimum quantity of acid was used, for it has already been shown that with less than the calculated quantity of acid the results are worthless.

Also in stability and in the ratio between its oxidizing value and its reducing value the solution shows exactly the behavior of a solution of hydrogen dioxide. There is, therefore, no reason for assuming the presence of any other substance. We may, therefore, consider the solution of potassium tetroxide to take place in the following way :

$$K_2O_4 + H_2SO_4 = K_2SO_4 + H_2O_2 + O_2.$$

According to this equation only one-third of the "per" oxygen would remain in the solution. The following experiments show this to be approximately true. The results are to be considered as only approximate, because the peroxide (sample B) contained a small amount of lower oxides of unknown nature, and also because the hydrogen dioxide may have been decomposed to a certain extent by local heating.

0.0755 gram was added slowly to an excess of dilute sulphuric acid cooled to 0°. The hydrogen dioxide was estimated with N/10 permanganate, of which 10.45 cc. were required, representing 0.00837 gram active oxygen. One-third of the total amount of "per" oxygen (32.8 per cent) is 0.00825 gram.

0.1390 gram, dissolved as before, required 19.7 cc. N/10 permanganate. The active oxygen, as hydrogen dioxide, is 0.01574 gram. Calculated, 0.01519 gram.

Harcourt[1] has obtained similar numbers by dissolving

[1] *Loc. cit.*

potassium tetroxide in dilute acid, although the solution was not cooled.

Sodium Dioxide.

Bach has also studied a solution of commercial sodium di-oxide and obtained results similar to those obtained with the solution of potassium tetroxide. These results I have like-wise been unable to verify. A sample of sodium dioxide ob-tained from Schuchardt, and which had not been previously opened, was used.

Analysis.—0.1243 gram was dissolved in water and the alkali estimated as with potassium tetroxide. 31.2 cc. $N/10$ HCl were required. Calculated for Na_2O_2, 31.8 cc.

0.1255 gram was dissolved in cold dilute sulphuric acid and the active oxygen estimated by means of potassium iodide and $N/10$ thiosulphate. Required, 30.3 cc. Calculated for Na_2O_2, 32.1 cc. Bach made no analysis of the sample which he used.

I. 2.5 grams were dissolved in 92 cc. of 1.09 normal sul-phuric acid, the temperature being kept at 0° during the solu-tion. (The calculated amount of 1.09 normal acid to dissolve and carry out the reaction with permanganate is 91 cc., based upon the analysis of the product.) Two cc. of this solution were removed and titrated with permanganate at 0°, as pre-viously described.

	cc.
Oxygen evolved (corrected)	13.5
$N/10$ $KMnO_4$ used	12.4
Oxygen calculated from $KMnO_4$	13.88

II. 2.5 grams were dissolved in 100 cc. of 2.9 normal sul-phuric acid which was kept at 0°. Two cc. of this solution gave :

	cc.
Oxygen (corrected)	13.48
$N/10$ $KMnO_4$ used	12.25
Oxygen calculated from $KMnO_4$	13.88

It is evident that exactly the same amount of oxygen was evolved as from a solution of hydrogen dioxide. From the solution of sodium dioxide Bach obtained an amount of oxy-gen which was 17 per cent higher than the amount calculated from the permanganate used.

It is possible that Bach's results are to be accounted for by the use of insufficient acid. With potassium tetroxide he used 50 cc. of normal acid to dissolve 3 grams. Whether more acid was added before the treatment with permanganate he does not say, and whether more is necessary cannot be told without knowing the purity of the tetroxide. An analysis of the latter is not given. Three grams of pure potassium tetroxide require 42.1 cc. of normal acid to neutralize the base. 25.3 cc. additional are necessary to carry out the reaction with permanganate, if the substance dissolves according to the equation previously given. This makes a total of 67.4 cc. necessary, while only 50 cc. were used.

With sodium dioxide, 100 cc. normal acid were used to dissolve 5 grams. If the dioxide were pure it would require 128 cc. of the same acid merely to neutralize it, and unless more acid were added before the treatment with permanganate the results would be worthless.

I have previously pointed out, under experiments with pure hydrogen dioxide, the result of the action of permanganate in the presence of insufficient acid. Granting that an insufficient quantity of acid was used, the excess of oxygen obtained by Bach was due to the catalytic action of the precipitated manganese dioxide upon the hydrogen dioxide remaining in the solution.

LABORATORY OF GENERAL CHEMISTRY,
    UNIVERSITY OF MICHIGAN,
        January 16, 1903.

CI.—ON DOUBLE AND TRIPLE THIOCYANATES OF CAESIUM, COBALT, AND SILVER.

BY F. L. SHINN AND H. L. WELLS.

As a continuation of some investigations by one of us and others on complex thiocyanates,[1] we have made a study of the caesium-cobalt, cobalt-silver, and caesium-cobalt-silver salts. The result is that we have found but a single compound in each case, although efforts were made to produce other combinations. The salts to be described are as follows:

[1] This JOURNAL, **28**, 254–284.

$Cs_2Co(SCN)_4.2H_2O$, color blue ;

$CoAg(SCN)_3.2H_2O$, color very dark-blue ;

and $Cs_2CoAg_2(SCN)_6.2H_2O$, color pink.

It is to be noticed that the first of these salts agrees in type with two double salts described in the previous communication from this laboratory, *viz.*,

$$Cs_2Mg(SCN)_4.2H_2O,$$

and $Cs_2Zn(SCN)_4.2H_2O.$

The cobalt-silver salt, however, does not correspond in type with the following bivalent metal-silver thiocyanates described in the article referred to :

$$ZnAg_2(SCN)_4 ;$$
$$BaAg_2(SCN)_4.2H_2O ;$$
$$SrAg_2(SCN)_4.2H_2O ;$$

and $CaAg_2(SCN)_4.2H_2O.$

The triple salt containing cobalt corresponds to the most common type of triple thiocyanates, of which the following were previously described :

$$Cs_2CaAg_2(SCN)_6.2H_2O ;$$
$$Cs_2MgAg_2(SCN)_6.2H_2O ;$$
$$Cs_2MnAg_2(SCN)_6.2H_2O ;$$
$$Cs_2NiAg_2(SCN)_6.2H_2O ;$$

and $Cs_2NiCu_2(SCN)_6.2H_2O.$

The pink color of the new triple salt, as compared with the intense blue colors of the two double salts, which are also hydrous, is worthy of attention, since this color shows that neither of the double salts probably exists as a component part of the triple salt. This argument strengthens the conclusion, reached in the previous article, that the triple salts are not compounds of two double salts.

EXPERIMENTAL PART.

For the work here described a solution of cobalt thiocyanate was prepared by dissolving cobalt carbonate in dilute thio-

cyanic acid. The latter was obtained by suspending lead thiocyanate (made by precipitation) in water, passing hydrogen sulphide into the liquid, filtering, and removing the excess of hydrogen sulphide by means of a current of air. The methods for preparing caesium thiocyanate have been mentioned in the previous article.

Caesium-Cobalt Thiocyanate, $Cs_2Co(SCN)_4.2H_2O$.—A solution containing about 40 grams of cobalt thiocyanate and gradually increasing quantities of caesium thiocyanate gave no crystals upon concentration, cooling and standing, until about 20 grams of the caesium salt had been added, when large, deep-blue crystals were obtained from a very syrupy solution (Analysis I.). A solution of 50 grams of caesium thiocyanate, to which cobalt thiocyanate was added in small portions, gave crystallizations of a blue salt which had the same appearance as the product mentioned above, but the crops were contaminated with crystals of caesium thiocyanate until about 35 grams of cobalt thiocyanate had been added, when a satisfactory crop was obtained (Analysis II.). Another sample was obtained from a solution containing about equal quantities of cobalt and caesium thiocyanates (Analysis III.). The results of the analyses are as follows:

	Calculated for $Cs_2Co(SCN)_4.2H_2O$.	I.	Found. II.	III.
Cs	44.85	44.35	....	....
Co	9.95	10.00	9.97	10.09
SCN	39.12	39.32	....	....
H_2O	6.07	....	....	....

Cobalt was determined as the metal by electrolysis of the ammoniacal sulphate solution. The caesium in the solution was then determined as sulphate. Sulphocyanogen was determined in a separate portion by the usual volumetric method.

The salt is stable in the air. When they are pulverized, the deep-blue crystals become brighter in color, and the powder loses water somewhat above 100° and becomes green. The anhydrous substance melts at about 170°.

Cobalt-Silver Thiocyanate, $CoAg(SCN)_3.2H_2O$.—This salt was obtained by saturating a hot, very concentrated solution

of about 40 grams of cobalt thiocyanate with silver thiocya-
nate and cooling. Only about 4 grams of the silver salt could
be dissolved in this operation, and when smaller quantities of
it were dissolved no double salt was obtained. Two separate
crops were made and analyzed, with the following results:

	Calculated for $CoAg(SCN)_3.2H_2O.$	Found.	
		I.	II.
Co	15.65	16.30	16.10
AgSCN	44.03	42.90	42.43
Sol. SCN	30.77	30.86	30.81
H_2O	9.55	....	....

For analysis the salt was decomposed by water, the result-
ing silver thiocyanate was collected and weighed in a Gooch
crucible, and the cobalt in the filtrate was determined by the
electrolysis of the ammoniacal sulphate solution. Sulpho-
cyanogen was determined volumetrically. The results on
cobalt came somewhat high and those on silver low, probably
on account of the great excess of cobalt thiocyanate in the
liquids from which the products were deposited.

The salt forms small, brilliant crystals which are stable in
the air and appear black by reflected light, but show a deep-
blue color by transmitted light. The powder has a brilliant
blue color. It loses water below 100° and changes its color
to dark-green. It may be mentioned here that the simple
salt, cobalt thiocyanate, undergoes very striking changes in
color when its solution is evaporated to dryness. The dilute
solution is pink, the concentrated solution is bright-blue, while
the dry salt is yellowish-brown. The last color, which is re-
markable for a cobalt salt, is mentioned by Meitzendorff.[1]

Caesium-Cobalt-Silver Thiocyanate, $Cs_2CoAg_2(SCN)_6.2H_2O.$
—When a concentrated solution containing about 20 grams
of cobalt thiocyanate and 5 grams of the caesium salt was
saturated with silver thiocyanate, only 2 or 3 grams of the lat-
ter went into solution, and no triple salt was formed upon
cooling. However, when the amount of caesium thiocyanate
in such a solution was increased to about 10 grams the triple
salt was formed, and it continued to be produced, and was
evidently more difficultly soluble in the liquid as the caesium
salt was gradually increased to 35 grams.

[1] Pogg. Ann., **56**, 77 (1842).

Three crops, made under different conditions, gave the following results upon analysis :

	Calculated for Cs$_2$CoAg$_2$(SCN)$_6$.2H$_2$O.	I.	Found. II.	III.
Cs	28.75	....	29.12	....
Co	6.38	6.55	....	6.99
AgSCN	35.89	35.22	35.12	35.08
Sol. SCN	25.08	25.20	....	25.16
H$_2$O	3.90	....	....	....

The salt forms thin, elongated plates of a bright-pink color. The color becomes somewhat violet when the crystals are air-dried, but there is no loss in brilliancy or transparency. The salt readily loses water considerably below 100°, changing its color to a dull dark-green. The anhydrous substance melts in the neighborhood of 180° to a transparent, bright-green liquid, which becomes dull violet upon solidifying and cooling. The salt is only slowly attacked by water, but after a time is completely decomposed by boiling water. It is very difficultly soluble in solutions of caesium and cobalt thiocyanates, and it cannot be recrystallized from water without the presence of an excess of these salts.

NEW HAVEN, CONN., Jan., 1903.

Contributions from the Sheffield Laboratory of Yale University.

CII.—ON SOME CONDENSATION-PRODUCTS OF THE PSEUDOTHIOUREAS : SYNTHESIS OF URA-CIL, THYMINE, AND SIMILAR COM-POUNDS.

By HENRY L. WHEELER AND HENRY F. MERRIAM.

Urea and thiourea have been shown to undergo condensation with a variety of substances, but apparently no one has attempted to use the simple pseudothioureas in any synthetic process whatever.[1]

The pseudothioureas in question, $HN=C(SR)-NH_2$, ($R=CH_3-$ or C_2H_5-), have not been isolated. Their halogen hydride salts result from the addition of alkyl halides to thiourea. These are described as extremely unstable compounds, and Claus[2] states that when the ethyl bromide addition-prod-

[1] Rathke has shown that their salts give guanidine when boiled with ammonia. Ber. d. chem. Ges., **17**, 309 (1884).

[2] Ann. Chem. (Liebig), **179**, 146 (1875).

uct is treated with alkali it decomposes into ethyl rhodanide, ammonia, and hydrogen bromide.

In the case of the methyl iodide addition-product, Bernthsen and Klinger[1] found that, with silver oxide, a solution containing a strong base resulted, which gave a blue color to red litmus. This base was supposed to be a hydroxyl compound, $H_2NCSNH_2.CH_3OH$, which, on evaporating in a desiccator, decomposed. The ethyl iodide addition-product, which Claus describes as an exceptionally unstable compound,[2] under similar treatment with silver oxide gave a strong alkaline solution which, on evaporation, contained cyanamide (dicyandiamide). A similar decomposition was observed when the compounds were treated with mercuric oxide.

We have made no attempts to isolate these free pseudothioureas, but, at first, in order to obtain an idea of their stability, we treated the methyl iodide addition-product in aqueous solution with an excess of alkali and benzoyl chloride, and obtained an excellent yield of the corresponding benzoylpseudothiourea,[3] $C_6H_5CON=C(SCH_3)-NH_2$. The ethyl bromide addition-product, on shaking with alkali and phenyl mustard oil, gave a good yield of the phenylpseudodithiobiuret,

$$C_6H_5NHCSN=C(SC_2H_5)NH_2.$$
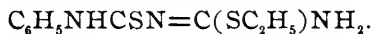
The free pseudothioureas are, therefore, not so unstable as one might be led to believe from previous work, and, owing to their strong basic nature, it seemed probable that they would undergo condensation with aldehyde and ketone esters more readily, and prove more reactive in general, than the normal ureas. This we have found to be the case.

Ernert[4] states that urea does not condense with the substituted acetoacetic esters or with benzoylacetic ester. Warmington,[5] also, was unable to obtain a condensation of urea and the latter ester, in aqueous solution, but found that they could be condensed in the dry state at a high temperature.

We have readily obtained such condensations with the

[1] Ber. d. chem. Ges., **11**, 493 (1878).
[2] *Ibid.*, **8**, 41 (1875).
[3] J. Am. Chem. Soc., **23**, 293 (1901).
[4] Ann. Chem. (Liebig), **258**, 362 (1890).
[5] J. prakt. Chem., [2], **47**, 202 (1893).

pseudothioureas at ordinary temperatures. These pyrimidine condensations, which are analogous to Pinner's,[1] take place in alkaline solution in a similar manner to that observed by Michael in the case of urea with acetoacetic and malonic esters.[2] They are also similar to Traube's synthesis of pyrimidine derivatives in which guanidine and ethyl cyanacetate are employed.[3]

A method similar to that of preparing methyluracil by condensing urea with acetoacetic ester, by means of hydrochloric acid,[4] has not been applied to the preparation of uracil, probably on account of the ease with which free formylacetic ester passes into trimesic ester. On the other hand, the sodium salt of formylacetic ester is not only easily prepared,[5] but is also quite stable, and we have found that it readily condenses, in aqueous solution, with both methyl- and ethylpseudothioureas, giving a good yield of the corresponding methyl- and ethyl-mercaptouracils. For example, with methylpseudothiourea, as follows :[6]

$$
\begin{array}{ccccc}
\text{NH}_2 & \text{C}_2\text{H}_5\text{OCO} & & \text{NH---CO} & \text{C}_2\text{H}_5\text{OH} \\
| & | & & | \quad | & \\
\text{CH}_3\text{S---C} \;+\; & \text{CH} \;=\; & \text{CH}_3\text{SC} & \text{CH} \;+\; & \\
\| & \| & \| \quad \| & \\
\text{NH} & \text{NaOCH} & \text{N------CH} & \text{NaOH}
\end{array}
$$
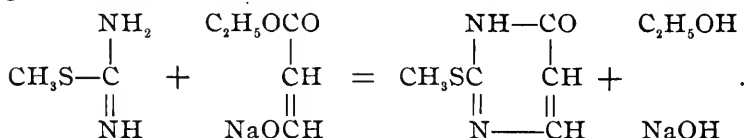
In order to obtain a practically quantitative yield of uracil from these compounds, heating with acids in a sealed tube is not necessary.[7] When they are boiled with concentrated hydrochloric acid, or better with hydrobromic acid, they evolve mercaptan and yield uracil as follows :

$$
\begin{array}{cccc}
\text{NHCO} & & \text{NH---CO} & \\
| \quad | & & | \quad | & \\
\text{RS---C} \quad \text{CH} \;+\; \text{H}_2\text{O} \;=\; & \text{OC} & \text{CH} \;+\; \text{RSH.} \\
\| \quad \| & & | \quad \| & \\
\text{N---CH} & & \text{NH---CH}
\end{array}
$$
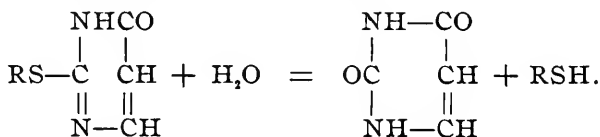
[1] "Die Imidoäther u. ihre Derivate," p. 209.

[2] J. prakt. Chem., **35**, 456 (1887).

[3] Ber. d. chem. Ges., **33**, 1371 (1900).

[4] Behrend : Ann. Chem. (Liebig), **229**, 9 ; **251**, 238.

[5] Wislicenus : Ber. d. chem. Ges., **20**, 2933 (1887).

[6] An attempt to condense urea with this salt gave a negative result.

[7] List has shown that 2-methylmercapto-4-methyluracil gives 4-methyluracil when heated with concentrated hydrochloric acid at 180°. Ann. Chem. (Liebig), **236**, 12 (1886).

Emil Fischer and Georg Roeder[1] have recently prepared uracil, thymine, and other pyrimidine derivatives by means of an interesting synthesis. Their method consists in heating urea with unsaturated acids and brominating the hydrouracils thus formed. The bromine derivatives are then converted into uracils by treatment with alkali or pyridine. This synthesis has the disadvantage that the unsaturated acids are not in all cases easily accessible compounds, and the yields, especially in the case of uracil, are below those obtained by our method.

Uracil prepared by our method agreed in all respects with the description given by Fischer and Roeder. We have found that sodium acetoacetic ester and pseudomethylthiourea give 2-methylmercapto-4-methyluracil, which List[2] has prepared by a different method. This, on boiling with hydrobromic acid, gave Behrend's[3] 4-methyluracil.

The isomeric 2-methylmercapto-5-methyluracil and 5-methyluracil, or thymine, were obtained in a similar manner. Free ethyl formylpropionate directly condensed with pseudomethylthiourea, and the sodium salt was also caused to react with the pseudothiourea :

$$
\begin{array}{cccc}
NH_2 & C_2H_5OCO & NH-CO & C_2H_5OH \\
| & | & |\quad| & \\
CH_3SC & + \quad C.CH_3 = CH_3SC \quad CCH_3 + & \\
|| & || & ||\quad|| & \\
NH & HOCH & N---CH & H_2O
\end{array}
$$
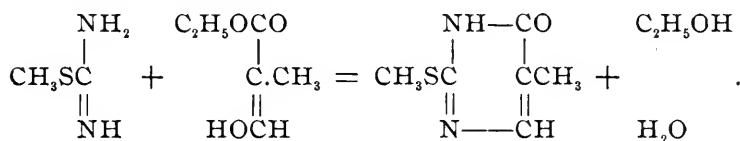
On boiling this mercapto derivative with hydrochloric acid we obtained thymine, which was identical in all respects with the natural product obtained from the nucleic acid of the spleen, a sample of which, through the kindness of Dr. P. A. Levene, was sent to us for comparison. When the samples were mixed the melting-point was not altered.

With the sodium salt of ethyl benzoylacetate and pseudomethylthiourea we obtained 2-methylmercapto-4-phenyluracil, which was converted by acids into 4-phenyluracil, identical with the phenyluracil described by Fischer and Roeder.

[1] Ber. d. chem. Ges., **34**, 3751 (1901).
[2] Ann. Chem. (Liebig), **236**, 12 (1886).
[3] *Ibid.*, **229**, 8.

With ethyl methylacetoacetate and pseudoethylthiourea we prepared 2-ethylmercapto-4,5-dimethyl-6-oxypyrimidine, which gave a new dimethyluracil (4,5-dimethyluracil) :

$$
\begin{array}{ccc}
\text{NH—CO} & & \text{NH—CO} \\
| \quad\quad | & & | \quad\quad | \\
\text{C}_2\text{H}_5\text{SC} \quad \text{CCH}_3 & \longrightarrow & \text{OC} \quad \text{CCH}_3. \\
\| \quad\quad \| & & | \quad\quad \| \\
\text{N —-CCH}_3 & & \text{NH — CCH}_3
\end{array}
$$
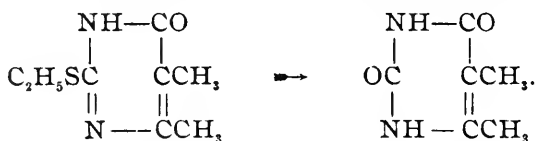
With ethyl ethyl-acetoacetate we prepared 2-methyl-mercapto-4-methyl-5-ethyl-6-oxypyrimidine and 4-methyl-5-ethyluracil. Like urea,[1] pseudomethylthiourea readily condenses with acetylacetone and two products are formed. It condenses also with ethyl cyanacetate.

Beside the above condensations, which involve an attachment to the two nitrogen atoms of the pseudothiourea, another type occurs in which only one nitrogen and the mercapto group take part. For example, amino acids react with the pseudothioureas in aqueous solution to form guanidine acids :

$$
\text{HN=C—(NH}_2\text{)—SR + H}_2\text{NCH}_2\text{COOH} =
$$
$$
\text{HN=C—(NH}_2\text{)—NHCH}_2\text{COOH + RSH.}
$$
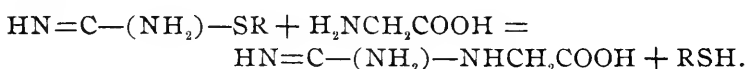
Since by appropriate treatment these compounds can be converted by loss of water into the corresponding rings, it seems probable that the isocreatinine obtained by Thesen[2] from fish flesh (haddock) may be prepared by this method, using N-methylpseudomethylthiourea and aminoacetic acid.

We wish to reserve the study of the condensation-products of the pseudothioureas for this laboratory.

EXPERIMENTAL PART.

Our experiments with the pseudothioureas have been confined to pseudomethyl- and pseudoethylthiourea.

Pseudomethylthiourea hydriodide was prepared by moistening finely powdered thiourea with alcohol and then adding an excess of methyl iodide. Heat was evolved so that a condenser was necessary. After standing twelve hours, ether

[1] Evans : J. prakt. Chem., **48**, 489 (1893).
[2] Hoppe-Seyler : Ztschr. physiol. Chem., **24**, 4 (1898).

was added and the residue filtered, washed with ether, and dried. The crude addition-product thus prepared was used in the following experiments.

Pseudoethylthiourea hydrobromide, for use in these condensations, can be conveniently prepared from thiourea containing considerable ammonium thiocyanate ; that is to say, from the product obtained by heating ammonium thiocyanate at 170° for forty-five minutes[1] and then crystallizing once or twice from water. The thiourea is powdered, moistened with alcohol, and an excess of ethyl bromide added. On boiling this mixture for four or five hours the greater part of the mass dissolves, leaving ammonium bromide as an insoluble residue. The solution is then filtered and most of the alcohol evaporated. The oil thus obtained is transferred to a distilling-bulb and the ethyl rhodanide distilled off under diminished pressure on the water-bath. The residue, on cooling, solidifies to a crystalline mass, which, after drying on paper in the air, melts at about 88° and is pure enough for use in the following experiments :

$$\begin{array}{cc} & \text{NHCO} \\ & | \quad | \\ \textit{2-Methylmercapto-6-oxypyrimidine,} \ \ \text{CH}_3\text{SC} & \text{CH.} \\ & || \quad || \\ & \text{N—CH} \end{array}$$ — In this
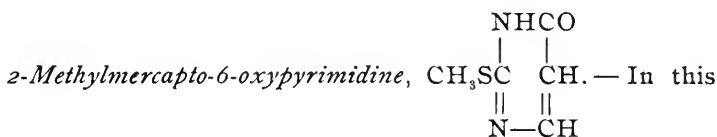
preparation the crude sodium salt of formylacetic ester[2] was considered as 70 per cent pure.[3]

Seven grams of sodium hydrate were dissolved in 70 cc. of water and 38 grams of the methyl iodide addition-product of thiourea were added, and then 29 grams of sodium formylacetic ester. The mixture was allowed to stand for twelve hours at ordinary temperature, then warmed on the water-bath for a few minutes, cooled, and acidified with acetic acid. The crystalline precipitate thus produced was filtered, washed, and dried. It weighed 11.3 grams, a yield of 46 per cent, calculating from the methyl iodide addition-product. It crystallized from water in long prisms, or short, lozenge-shaped

[1] Reynolds and Werner : J. Chem. Soc. (London), **83,** 1 (1903).

[2] Wislicenus : Ber. d. chem. Ges., **20,** 2933.

[3] Von Pechmann : *Ibid.,* **25,** 1047.

tablets, and the surfaces of the crystals were generally etched. It is quite soluble in alcohol and acetone, and it melts at 198° to 199°. A nitrogen determination gave :

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.72	19.86

2-Ethylmercapto-6-oxypyrimidine,
$$C_2H_5SC\begin{matrix} NH{-}CO \\ | \quad\quad | \\ CH. \\ || \quad\quad || \\ N{-}{-}CH \end{matrix}$$
— Fifty-nine grams of the ethyl bromide addition-product of thiourea were treated with one molecular proportion of sodium hydrate in 10 per cent aqueous solution, and then 40 grams of formyl-acetic ester were added. After standing for twenty-four hours the solution was divided into two equal portions. One, after warming on the water-bath until effervescence stopped, was cooled and immediately acidified with acetic acid. This gave 6.3 grams of the mercapto derivative. The other portion was allowed to stand for a week. On acidifying then, 6.1 grams of the mercapto compound were obtained, a yield of 32 per cent of the calculated. In another experiment 25 grams of the ethyl bromide addition-product were dissolved in more dilute alkali, namely, 5.5 grams of sodium hydrate in 95 cc. of water, and 27 grams of sodium formylacetic ester were added. After two hours' standing, one-half of the solution was warmed, cooled, and acidified with acetic acid, whereupon 5 grams of the mercapto compound separated. After standing two days the remaining portion gave 4.9 grams of the condensation-product, a yield of 47 per cent of the calculated.

It is evident from this that the materials react in a short time, and that long standing does not influence the yield. The reaction possibly involves an addition similar to that in the case of acetoacetic ester and urea[1], since it frequently happens that these mixtures can stand for several days, and then, if the solution is not warmed before acidifying, no precipitation whatever occurs. Moreover, the fact that usually a yield

[1] Behrend and Ernert : Ann. Chem. (Liebig), **258**, 360 (1890).

approximating only one-half the calculated is obtained may also possibly be accounted for by the assumption that, like urea and acetoacetic ester in alkaline solution, 2 molecules of the ester react with only one of the pseudothiourea.

In one experiment, however, 5 grams of the ethyl bromide addition-product, 1.1 grams of sodium hydrate, and 6 grams of the sodium salt in 10 cc. of water, on standing over night, gave 2.9 grams of the condensation-product, a yield of 68.8 per cent of the calculated. On crystallizing from 10 cc. of alcohol, 1.75 grams of pure ethylmercaptooxypyrimidine separated at once. This substance is easily soluble in warm alcohol and hot water, difficultly soluble in cold, and forms beautiful, colorless, small, stout prisms and pyramids melting at 152°. A nitrogen determination gave:

	Calculated for $C_6H_8ON_2S$.	Found.
N	17.94	17.93

Uracil,
$$\begin{array}{ccc} \mathrm{NH} & - & \mathrm{CO} \\ | & & | \\ \mathrm{OC} & & \mathrm{CH.} \\ | & & \| \\ \mathrm{NH} & - & \mathrm{CH} \end{array}$$
—Fifteen grams of the above methyl-mercaptouracil and 150 cc. of concentrated hydrochloric acid were boiled for four hours, when mercaptan had ceased being evolved. The solution was evaporated to dryness and the residue, after drying, weighed 11.9 grams (94.4 per cent yield). It melted with effervescence at 335° (on an Anschütz thermometer in a paraffin-bath), and, on crystallizing from water, it formed balls of minute, pure-white needles, which, on rapidly heating, melted at 338°. By holding the temperature a few degrees below this the material could be made to melt. It agreed in properties with Fischer and Roeder's[1] preparation. When the ethylmercapto derivative (1.5 grams) was heated in a closed tube with concentrated hydrochloric acid (5 cc.) for four and one-half hours, about 0.05 gram of an insoluble by-product was formed, and 0.9 gram of pure uracil was obtained. A nitrogen determination gave:

[1] *Loc. cit.*

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.00	25.24

One hundred parts of water at 25° dissolve 0.358 part of uracil.

Uracil may be boiled with alkali and recovered unaltered by acidifying the solution. The alkaline solution probably contains the substance as a salt of β-uramidoacrylic acid, just as Behrend's methyluracil gives β-uramidocrotonic acid. When uracil is dissolved in ammonia and most of this removed by boiling, then silver nitrate is added and the solution is boiled, an amorphous silver salt is precipitated, which is soluble in an excess of ammonia and nitric acid. The composition of the salt prepared in this manner varied. One preparation gave 63.8 and 64 per cent silver, another 59.9 and 60.1 per cent silver, while the calculated for silver β-uramidoacrylate is 62.79 per cent. Uracil does not form a picrate.

5-Bromuracil.—Two and one-half grams of uracil were suspended in carbon disulphide and 3.8 grams of bromine were added. Hydrogen bromide was slowly evolved, and after two days, on evaporating to dryness, a red residue was obtained which, on warming on the water-bath, became colorless. When crystallized from water it formed small, stout, colorless prisms, and when heated turned dark above 200°, and melted with some effervescence at about 293°. A nitrogen determination gave :

	Calculated for $C_4H_3O_2N_2Br$.	Found.
N	14.66	14.60

2-Methylmercapto-4-methyl-6-oxypyrimidine,

$$\begin{array}{ccc} NH & - & CO \\ | & & | \\ CH_3SC & & CH \\ \| & & \cdot\| \\ N & - & CCH_3 \end{array}$$
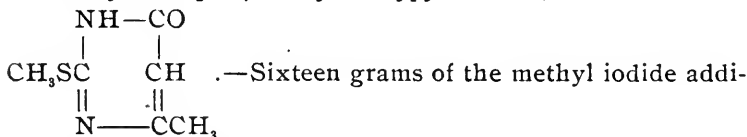
.—Sixteen grams of the methyl iodide addition-product of thiourea were dissolved in 20 cc. of water and added to a cold 30 per cent solution of 4.5 grams of potassium hydrate. Nine and six-tenths grams of acetoacetic ester were then added and the mixture allowed to stand. The

next day long prisms had formed. After two days these were
filtered and found to weigh 5 grams. This material was sol-
uble in acids and alkali, and it melted at 219°, the melting-
point assigned to this compound by List. When 2 grams of
this were boiled with 10 cc. of hydrobromic acid for one hour
mercaptan was given off and 1.2 grams of Behrend's 4-methyl-
uracil were obtained.

2-Methylmercapto-5-methyl-6-oxypyrimidine,

$$
\begin{array}{cc}
\text{NH} & \!\!\!\!-\text{CO} \\
| & \quad | \\
\text{CH}_3\text{SC} & \quad \text{CCH}_3. \\
\| & \quad \| \\
\text{N} & \!\!\!\!-\!\!-\text{CH}
\end{array}
$$
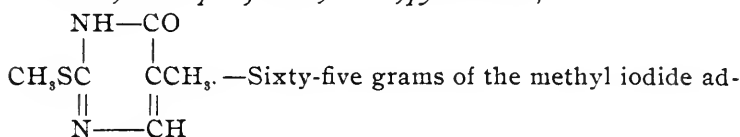
—Sixty-five grams of the methyl iodide ad-
dition-product of thiourea were treated with 17 grams of
potassium hydrate in 150 cc. of water, and 45 grams of sodium
formylpropionic ester were then added. The mixture, on
standing two and a half days, was filtered from some sedi-
ment and neutralized with acetic acid. A fine crystalline
precipitate of methylmercaptothymine came down, which
weighed 9.2 grams, or 20 per cent of the calculated. It crys-
tallized in strings of small plates from water, in which it is
difficultly soluble when hot and nearly insoluble when cold.
On heating, it sintered at about 225° and melted at 233°. A
nitrogen determination gave :

	Calculated for $C_6H_8ON_2S$.	Found.
N	17.94	17.95

5-Methyluracil (Thymine),

$$
\begin{array}{cc}
\text{NH} & \!\!\!\!-\text{CO} \\
| & \quad | \\
\text{OC} & \quad \text{CCH}_3. \\
| & \quad \| \\
\text{NH} & \!\!\!\!-\text{CH}
\end{array}
$$
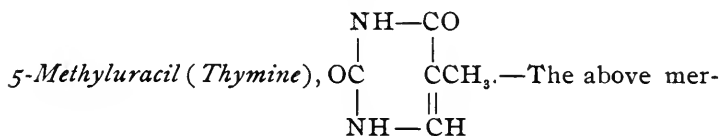
—The above mer-
captothymine reacted less readily with hydrochloric acid than
in the other cases. Nine and two-tenths grams were boiled
with 100 cc. of concentrated hydrochloric acid for ten hours,
whereupon no more mercaptan was given off. The solution, on
evaporating, then gave 7.3 grams of crude thymine (melting at
319°), which is 99 per cent of the calculated. This crystal-
lized from water in small, apparently rectangular, colorless

plates, and on rapidly heating melted at 326° (on an An-schütz thermometer). Fischer and Roeder state that their preparation sintered at 318° and melted at 321°. A sample of thymine which Dr. P. A. Levene, of the Pathological Institute at Ward's Island, N. Y., kindly gave us, proved to be identical with our compound. This sample was obtained from the nucleic acid of the spleen, and on mixing it with some of our substance the melting-point was unchanged. A nitrogen determination in the case of the synthetic product gave :

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.36

One hundred parts of water at **25°** dissolve 0.404 part of thymine.

2-Ethylmercapto-4,5-dimethyl-6-oxypyrimidine,

$$
\begin{array}{l}
\text{NH——CO} \\
\ \mid \qquad\ \ \mid \\
\text{C}_2\text{H}_5\text{SC} \quad \text{CCH}_3. \\
\ \ \parallel \qquad \parallel \\
\text{N——CCH}_3
\end{array}
$$ —Six grams of potassium hydrate were
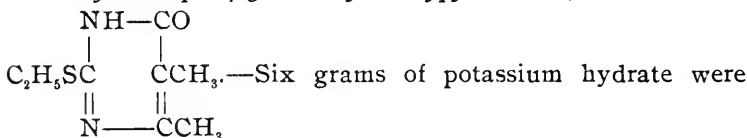
dissolved in 50 cc. of water and cooled. To this was added 13 grams of the ethyl bromide addition-product of thiourea and then 10 grams of methyl acetoacetic ester. The oil gradually disappeared and a white solid was formed. After standing for two days the solution was made slightly acid with hydrochloric acid and filtered. The precipitate in this case proved to be a mixture. On boiling with about 30 cc. of alcohol and filtering while hot, a separation was effected. The soluble portion was crystallized from a mixture of alcohol and ether. It formed stout prisms melting at about 156°, sintering at about 151,° and a nitrogen determination gave :

	Calculated for $C_8H_{12}ON_2S$.	Found.
N	15.2	15.6

The compound that was not readily dissolved by boiling alcohol was purified by crystallizing it from a large amount of alcohol. It was found to be free from sulphur, and on heating it began to decompose at about 260°, and effervesced at 269° to 270°, turning reddish-brown. It consisted of minute,

microscopic crystals that formed twins having the form of a cross. We did not stop to determine the structure of this compound, but we believe that possibly it is acetomethylacetylcyanamide, $CH_3CO(CH_3)CHCONHCN$. A nitrogen determination agreed with the calculated for this formula.

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	20.03

4,5-Dimethyluracil,
$$\begin{array}{c} NH-CO \\ | \quad\quad | \\ OC \quad\quad CCH_3. \\ | \quad\quad || \\ NH-CCH_3 \end{array}$$
—About 1 gram of the above ethylmercaptodimethyluracil was boiled for four hours with 10 cc. of concentrated hydrochloric acid. Mercaptan was given off and there was a smooth decomposition into the oxygen derivative. The solution was evaporated to dryness and the residue was crystallized twice from alcohol. It crystallized in microscopic needles which melted to a clear liquid, with partial decomposition, at 292°. A nitrogen determination gave :

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	20.34

2-Methylmercapto-4-methyl-5-ethyl-6-oxypyrimidine,
$$\begin{array}{c} NH-CO \\ | \quad\quad | \\ CH_3SC \quad\quad C.C_2H_5. \\ || \quad\quad || \\ N --- C.CH_3 \end{array}$$
—Ten grams of the methyl iodide addition-product of thiourea were dissolved in a solution of 2.6 grams of potassium hydrate (1 molecule) in 20 cc. of water, and to this 7 grams of ethyl ethylacetoacetate were added. A little alcohol was also added, and finally some more alkali, and the mixture was allowed to stand for a week. Solid material gradually separated, which was filtered after neutralizing the solution. The yield of crude material was 3.2 grams. It was crystallized from alcohol, from which it separated in long, flat, colorless prisms with branching, brush-like

ends. It sintered at 201° to 202° and melted at about 203° with slight effervescence. It was fairly soluble in hot alcohol and very difficultly soluble in water. A nitrogen determination gave:

	Calculated for $C_6H_{12}ON_2S$.	Found.
N	15.22	15.26
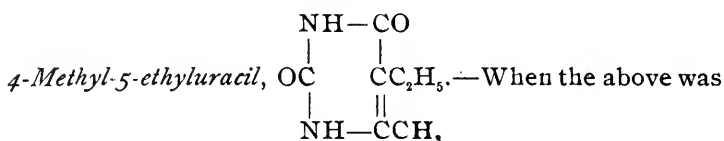
4-Methyl-5-ethyluracil,
$$\begin{array}{c} NH-CO \\ | \quad\quad | \\ OC \quad\quad CC_2H_5. \\ | \quad\quad || \\ NH-CCH_3 \end{array}$$
—When the above was boiled for three hours with hydrobromic acid and evaporated a syrup was obtained, which solidified on treating with alcohol. After six crystallizations from alcohol it melted constantly at 237°, sintering at about 230°. It formed irregular, colorless leaflets. A nitrogen determination gave:

	Calculated for $C_7H_{10}O_2N_2$.	Found.
N	18.18	17.86

2-Methylmercapto-4-phenyl-6-oxypyrimidine,
$$\begin{array}{c} NH-CO \\ | \quad\quad | \\ CH_3SC \quad\quad CH \\ || \quad\quad || \\ N \!-\! CC_6H_5 \end{array}$$
—Fifteen grams of the methyl iodide addition-product of thiourea were dissolved in a solution of 8 grams of potassium hydrate in 40 cc. of water, and 12 grams of benzoylacetic ester were then added. After the mixture was allowed to stand for two days it was acidified and the precipitate crystallized from alcohol, whereupon 3.5 grams of material crystallizing in long, slender needles, melting at 240°, were obtained. A nitrogen determination gave:
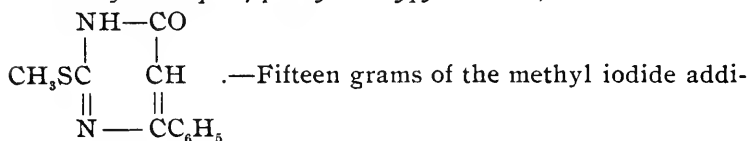
	Calculated for $C_{11}H_{10}ON_2S$.	Found.
N	12.89	12.74

4-Phenyluracil,
$$\begin{array}{c} NH-CO \\ | \quad\quad | \\ OC \quad\quad CH \\ | \quad\quad || \\ NH-C.C_6H_5 \end{array}$$
—A small amount of the above
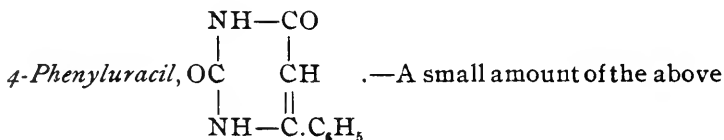
methylmercaptophenyloxypyrimidine was heated with con-
centrated hydrochloric acid for two hours. It gradually went
into solution and then separated in crystalline form. The
solution was evaporated to dryness and the residue was crys-
tallized from alcohol. The crystals were in the form of
microscopic prisms and melted at 269° to 270°. Fischer and
Roeder state that their phenyluracil formed microscopic
needles melting at 267° (corr.).

Guanidineacetic acid[1] (*Glycocyamine*) was formed when 12.2
grams of the methyl iodide addition-product of thiourea were
dissolved in 15 cc. of water containing 3.2 grams of potassium
hydrate, and then a concentrated solution of 5 grams of
amidoacetic acid were added. Mercaptan began to come off
immediately, the mixture evolved heat, and crystals separa-
ted. These were fairly soluble in water, and formed rectangu-
lar plates which decomposed between 250° to 260° without
melting. A nitrogen determination gave :

	Calculated for $C_3H_7O_2N_3$.	Found.
N	35.89	36.07

The *picrate* separated from an aqueous solution in long,
bright-yellow needles, melting with decomposition at about
202°. It was very soluble in hot water and sparingly in cold.
A nitrogen determination gave :

	Calculated for $C_9H_{10}O_9N_6$.	Found.
N	24.27	24.00

Orthoguanidinebenzoic acid was obtained when 8 grams of
the methyl iodide addition-product of thiourea were added to
an aqueous solution of 5 grams of anthranilic acid and 2 grams
of potassium hydrate. The material was practically insoluble
in water, alcohol, and benzene, and did not melt at 260°. A
nitrogen determination gave :

	Calculated for $C_8H_9O_2N_3$.	Found.
N	23.46	23.70

When this substance was dissolved in aqueous sodium hy-

[1] Strecker : Jsb., 1861, 530; Nencki and Sieber : J. prakt. Chem., [2], **17**, 477.

drate, and precipitated with carbon dioxide, it gave *o*-benz-glycocyamidine.[1]

Pseudomethylthiourea Chloracetate,
H_2N—$C(SCH_3)$=$NH.ClCH_2COOH$.—Thirty-three grams of the methyl iodide addition-product of thiourea were dissolved in a small quantity of cool alcohol, and a concentrated alcoholic solution of 8.5 grams of potassium hydrate was added. The solution was filtered from potassium iodide and then 14.5 grams of chloracetic acid were slowly added. Crystalline material soon separated which, on drying, weighed 17 grams. When crystallized from alcohol it formed transparent, rectangular plates, melting at 162°. It was very soluble in water. A nitrogen determination gave:

	Calculated for $C_4H_9O_2N_2SCl$.	Found.
N	15.17	15.26

NEW HAVEN, CONN., Feb. 26, 1903.

CIII.—SYNTHESES OF AMINOOXYPYRIMIDINES HAVING THE COMPOSITION OF CYTOSINE : 2-AMINO-6-OXYPYRIMIDINE AND 2-OXY-6-AMINOPYRIMIDINE.

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

The interest which in recent years has been attached to the study of pyrimidine derivatives has been increased by a new discovery of Kossel and Steudel. Working with a large quantity of sturgeons' testicles they obtained, in the histidine fraction, a basic substance agreeing in composition with the formula $C_4H_5ON_3$. Kossel and Steudel state their belief that this compound is an aminooxypyrimidine,[2] since hitherto all of the nitrogen compounds obtained from nucleic acid have been found to contain the pyrimidine ring. This new substance was found to closely resemble cytosine, which Kossel and Neumann[3] obtained in the year 1894 as a cleavage-prod-

[1] Griess : Ber. d. chem. Ges., **13**, 977.
[2] Ztschr. physiol. Chem., **37**, 179 (1902).
[3] Ber. d. chem. Ges., **27**, 2215 (1894).

uct of thymus nucleic acid. Kossel and Steudel have recently
undertaken the reinvestigation of thymus cytosine and they
now[1] conclude that the product is identical with sturgeon
cytosine. They state that it can also be prepared from her-
rings' testicles and call attention to the fact of its wide occur-
rence in animal organs.

Dr. P. A. Levene has kindly sent us the proof of his article
on " Darstellung und Analyse einiger Nucleinsäuren," in
which he describes the preparation of this base from the
nucleic acid of the spleen and pancreas.[2]

Kossel and Steudel[3] conclude that material yielding uracil is
widely disseminated in animal organs, and it seemed probable
that perhaps uracil results from the cleavage of cytosine by
treatment with sulphuric acid at high temperatures. More-
over, they state in their last paper[4] that cytosine, by the action
of nitrous acid, gives a substance having the properties of
uracil.

From this it appears that of the seven theoretically possible[5]
aminooxypyrimidines, the first to be considered are those that
would be expected to yield uracil by the above treatment.
An examination of the following formulas will show that for-
mulas I. and II. are the only ones that agree with this be-
havior :

$$
\begin{array}{ccc}
\text{N}\mathop{=\!=\!=}\text{C}\text{---}\text{NH}_2 & \text{NH}\text{---}\text{CO} & \text{NH}\text{---}\text{CH} \\
| \qquad | & | \qquad | & | \qquad \| \\
\text{CO} \quad \text{CH} & \text{H}_2\text{N}\text{---}\text{C} \quad \text{CH} & \text{CO} \quad \text{C}\text{---}\text{NH}_2 \\
| \qquad \| & \| \qquad \| & | \qquad | \\
\text{NH}\text{---}\text{CH} & \text{N}\text{------}\text{CH} & \text{N}\mathop{=\!=\!=}\text{CH} \\
\text{I.} & \text{II.} & \text{III.}
\end{array}
$$

$$
\begin{array}{ccc}
\text{NH}\text{---}\text{CO} & \text{NH}\text{---}\text{CO} & \text{N}\mathop{=\!=\!=}\text{CH} \\
| \qquad | & | \qquad | & | \qquad | \\
\text{HC} \quad \text{C}\text{---}\text{NH}_2 & \text{HC} \quad \text{CH} & \text{HC} \quad \text{COH} \\
\| \qquad \| & \| \qquad \| & \| \qquad \| \\
\text{N}\text{------}\text{CH} & \text{N}\text{------}\text{C}\text{---}\text{NH}_2 & \text{N}\text{---}\text{C}\text{---}\text{NH}_2 \\
\text{IV.} & \text{V.} & \text{VI.}
\end{array}
$$
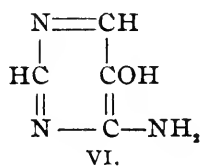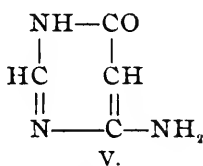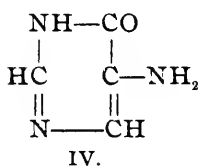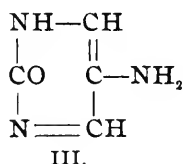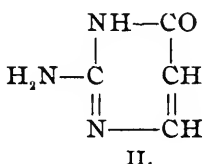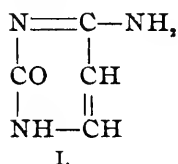
[1] Ztschr. physiol. Chem., **37**, 379 (1903).

[2] To appear in Ztschr. physiol. chem., **38**, (1903). See also Am. J. Physiol., **8**,
XII (1903); J. Am. Chem. Soc., **25**, R. 188 (1903).

[3] *Ibid.*, **37**, 247 (1903).

[4] *Ibid.*, **37**, 380 (1903).

[5] Tautomeric forms are not considered.

$$\begin{array}{ccc}
& \text{N} \!\!-\!\!-\!\! \text{CH} & \\
& \| \qquad \| & \\
\text{H}_2\text{N} \!\!-\!\! \text{C} & \qquad \text{COH} & \\
& | \qquad | & \\
& \text{N} \!\!=\!\!=\!\! \text{CH} &
\end{array}$$

VII.
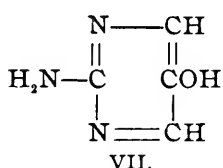
We have now prepared the two aminooxypyrimidines represented by formulas I. and II. and we find that both products agree closely in properties with the descriptions of cytosine. Of the two compounds, 2-oxy-6-amino-pyrimidine, formula I., agrees better than the isomer, 2-amino-6-oxypyrimidine. Formula II., in fact, seems to be excluded as representing cytosine chiefly because this compound crystallizes from water in anhydrous crystals. Its picrate melts a little higher than the melting-point given for cytosine picrate, but in other respects the salts are closely similar.

On the other hand, 2-oxy-6-aminopyrimidine crystallizes with 1 molecule of water of crystallization, like cytosine, and its properties agree in practically every respect, as far as can be judged, with the descriptions of the natural substance. The picrate, when prepared from the pure base, has a higher decomposing-point than that given for the picrate from natural cytosine. However, we are inclined to believe that our base and cytosine are identical and, therefore, the structure of cytosine is to be represented by formula I.[1] It will be necessary to compare our material with the natural before this can be definitely settled, and we hope soon to obtain a sample of the natural substance.

When 2-oxy-6-aminopyrimidine was heated with 20 per cent sulphuric acid for 3 hours at 150°-170° it was found that 15 per cent of the material was converted into uracil. Dr. Osborne informs us that to obtain uracil it was necessary to heat triticonucleic acid with acids for a considerable time.[2]

Since uracil results from the cleavage-cytosine, the natural

[1] The substance can naturally be viewed as 2-oxy-4-aminopyrimidine, and, on account of the usual nomenclature, this aspect better illustrates its character as a sort of hydrated fragment of uric acid. Its relation to uracil, however, is better shown by representing the substance as a 6-amino derivative or the tautomeric 6-imino form.

[2] See Report Conn. Agr. Expt. Sta. for 1901 p. 409.

assumption is that the analogous thymine, which until recently has been more widely obtained as a cleavage-product, results from the decomposition of a corresponding base, the as yet undiscovered 5-methylcytosine, this base undergoing cleavage more readily than cytosine. We intend to give an account of this new base later, the preparation of these bases being one of the first steps toward the synthesis of the nucleic acids.

We prepared the synthetic cytosine as follows : The ethyl bromide addition-product of thiourea was treated with 1 molecule of alkali in aqueous solution and the sodium salt of ethyl formylacetate added. On standing a number of hours, then warming for a few minutes, cooling, and acidifying with acetic acid, 2-ethylmercapto-6-oxypyrimidine was obtained :

$$
\begin{array}{ccccc}
\mathrm{NH_2} & \mathrm{C_2H_5OCO} & & \mathrm{NH{-}CO} & \mathrm{C_2H_5OH} \\
| & | & & | \quad\ | & \\
\mathrm{C_2H_5SC} + & \mathrm{CH} = & \mathrm{C_2H_5SC} & \mathrm{CH} + & \\
\| & \| & & \| \quad\ \| & \\
\mathrm{NH} & \mathrm{NaOCH} & & \mathrm{N{-}{-}CH} & \mathrm{NaOH}
\end{array}
$$
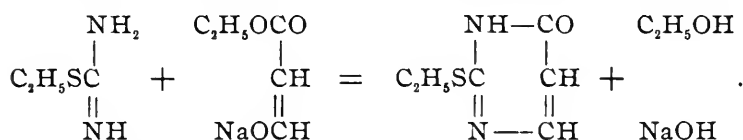
The 2-ethylmercapto-6-oxypyrimidine was converted into 2-ethylmercapto-6-chlorpyrimidine by means of phosphorus pentachloride and the phosphorus oxychloride was removed by evaporation in a vacuum.

$$
\begin{array}{cccc}
\mathrm{NH{-}CO} & & \mathrm{N{=}{=}CCl} & \\
| \quad\ | & & | \quad\ | & \\
\mathrm{C_2H_5SC} & \mathrm{CH} + \mathrm{PCl_5} = \mathrm{C_2H_5SC} & \mathrm{CH} + \mathrm{POCl_3} + \mathrm{HCl}. \\
\| \quad\ \| & & \| \quad\ \| & \\
\mathrm{N{-}{-}CH} & & \mathrm{N{-}{-}CH} &
\end{array}
$$
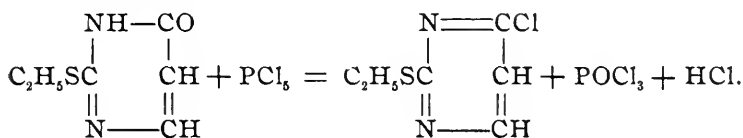
When 2-ethylmercapto-6-chlorpyrimidine was heated with alcoholic ammonia it gave 2-ethylmercapto-6-aminopyrimidine.

$$
\begin{array}{cccc}
\mathrm{N{=}{=}CCl} & & \mathrm{N{=}{=}C{-}NH_2} & \\
| \quad\ | & & | \quad\ | & \\
\mathrm{C_2H_5SC} & \mathrm{CH} + 2\mathrm{NH_3} = \mathrm{C_2H_5SC} & \mathrm{CH} \\
\| \quad\ \| & & \| \quad\ \| & \\
\mathrm{N{-}{-}CH} & & \mathrm{N{-}{-}CH} &
\end{array}
$$
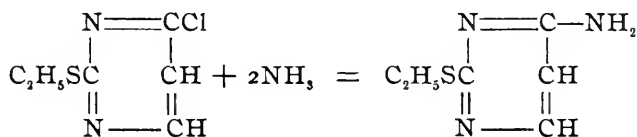
Finally the 2-ethylmercapto-6-aminopyrimidine was converted into the 2-oxy-6-aminopyrimidine by boiling with hydrobromic acid :

$$
\begin{array}{ccc}
\mathrm{N}\!=\!\!=\!\mathrm{C}\!-\!\mathrm{NH_2} & & \mathrm{N}\!=\!\!=\!\mathrm{C}\!-\!\mathrm{NH_2} \\
\mid \qquad \mid & & \mid \qquad \mid \\
\mathrm{C_2H_5SC} \quad \mathrm{CH} \;+\; \mathrm{H_2O} \;=\; \mathrm{OC} \quad \mathrm{CH} \;+\; \mathrm{C_2H_5SH.} \\
\parallel \qquad \parallel & & \mid \qquad \parallel \\
\mathrm{N}\!-\!\!-\!\mathrm{CH} & & \mathrm{NH}\!-\!\mathrm{CH}
\end{array}
$$
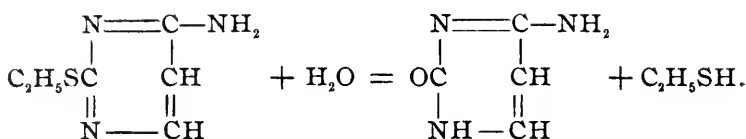
The synthesis of 2-amino-6-oxypyrimidine was effected by treating sodium formylacetic ester with free guanidine in aqueous solution, whereupon the following condensation took place :

$$
\begin{array}{ccccc}
\mathrm{NH_2} & \mathrm{C_2H_5OCO} & & \mathrm{NH}\!-\!\mathrm{CO} & \mathrm{C_2H_5OH} \\
\mid & \mid & & \mid \qquad \mid & \\
\mathrm{H_2N}\!-\!\mathrm{C} \;+\; & \mathrm{CH} \;=\; & \mathrm{H_2N}\!-\!\mathrm{C} & \mathrm{CH} \;+\; & \\
\parallel & \parallel & & \parallel \quad \parallel & \\
\mathrm{NH} & \mathrm{NaOCH} & & \mathrm{N}\!-\!\!-\!\mathrm{CH} & \mathrm{NaOH}
\end{array}
$$
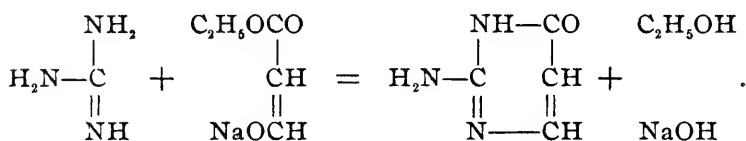
Sodium formylacetic ester is easily prepared by treating equal weights of ethyl formate and ethyl acetate, in two volumes of ether, with metallic sodium, according to the directions of Wislicenus.[1]

<div align="center">EXPERIMENTAL PART.</div>
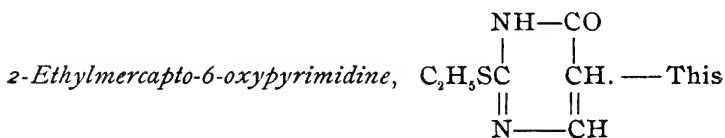
2-Ethylmercapto-6-oxypyrimidine,
$$
\begin{array}{c}
\mathrm{NH}\!-\!\mathrm{CO} \\
\mid \qquad \mid \\
\mathrm{C_2H_5SC} \quad \mathrm{CH.} \\
\parallel \qquad \parallel \\
\mathrm{N}\!-\!\!-\!\mathrm{CH}
\end{array}
$$
—— This compound has been described in the preceding article by Wheeler and Merriam. We have usually taken 50 grams of the ethyl bromide addition-product of thiourea,[2] dissolved in 10 per cent sodium hydrate, and have then added somewhat over the calculated quantity of dry sodium ethyl formylacetate. After standing for two or three hours the solution, heated to boiling and then cooled, was acidified with acetic acid. A yield of about 48 per cent of the calculated of crude mercaptooxypyrimidine was usually obtained.

2-Ethylmercapto-6-chlorpyrimidine,
$$
\begin{array}{c}
\mathrm{N}\!=\!\!=\!\mathrm{CCl} \\
\mid \qquad \mid \\
\mathrm{C_2H_5SC} \quad \mathrm{CH.} \\
\parallel \qquad \parallel \\
\mathrm{N}\!-\!\!-\!\mathrm{CH}
\end{array}
$$
— When
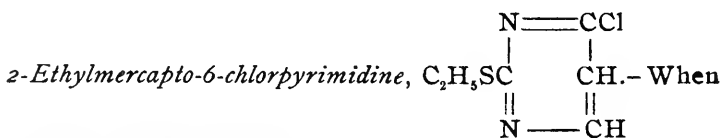
[1] Ber. d. chem. Ges., **20**, 2933 (1887).
[2] Claus : Ann. Chem. (Liebig), **179**, 145.

2-ethylmercapto-6-oxypyrimidine (5.3 grams) and phosphorus pentachloride (7.5 grams) were warmed on the steam-bath they reacted smoothly and hydrogen chloride was given off. The product was an oil. An attempt to purify it by distilling off the phosphorus oxychloride at ordinary pressure in an oil-bath, at 150°, caused decomposition. It was found that the oil could be distilled in steam, but the greater part was converted into uracil by this treatment. The portion purified in this manner (2 grams) was analyzed with the following result :

	Calculated for $C_6H_7N_2SCl$.	Found.
N	16.04	16.8

The oil, when dry, is stable at 150°. When boiled with hydrochloric acid it gives uracil. The chlorpyrimidine, for conversion into the amino derivative, was prepared as follows : 6.3 grams of 2-ethylmercapto-6-oxypyrimidine and 8.5 grams of phosphorus pentachloride were heated on the steam-bath until the action was complete. The phosphorus oxychloride was removed by heating in an oil-bath at 140°, under a pressure of 12 mm., for about fifteen minutes. The crude oil thus obtained weighed 6.5 grams, a yield of 92 per cent of the calculated. In another preparation 15.5 grams of the 2-ethylmercapto-6-oxypyrimidine gave 15.5 grams of chlorine compound, or 90 per cent of the calculated.

2-Ethylmercapto-6-aminopyrimidine, C_2H_5SC

$$\begin{array}{ccc} N\!\!=\!\!\!=\!\!C\!\!-\!\!NH_2 \\ | \qquad | \\ C_2H_5SC \qquad CH \\ \| \qquad \| \\ N\!\!-\!\!\!-\!\!CH \end{array}$$.—
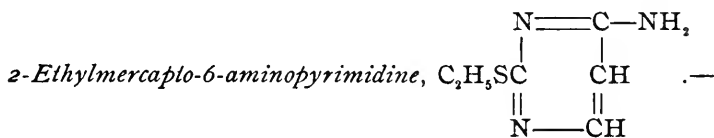
When 2-ethylmercapto-6-chlorpyrimidine (6.5 grams) was heated in a closed tube with alcoholic ammonia at 140° to 150°, for six hours, the action was complete. An odor of mercaptan was apparent on opening the tube, showing too energetic treatment, and ammonium chloride had separated. The alcohol was removed by evaporation, after filtering from ammonium chloride, and the dark varnish which was obtained was washed with a few cubic centimeters of cold water. By this treatment the material completely solidified to a hard

cake. It was very soluble in alcohol and in benzene, and fairly soluble in hot water. The weight of the crude product was 4.7 grams, a yield of 82 per cent of the calculated. The base dissolved immediately in dilute hydrochloric acid and was precipitated by ammonia in stout tables. It was purified by boiling in alcohol with animal charcoal and then crystallizing from 50 per cent alcohol. It separated in the form of colorless plates and melted at 85° to 86°. A nitrogen determination gave :

	Calculated for $C_6H_9N_3S$.	Found.
N	27.1	27.6

In another preparation the chlorpyrimidine was heated with alcoholic ammonia at 115° to 120° for five and a half hours. From 15.5 grams of the chlorine compound 11.6 grams of the base were obtained, which is a yield of 84 per cent of the calculated.

$$\text{Cytosine or 2-Oxy-6-aminopyrimidine,} \quad
\begin{array}{ccc}
N & \!\!\!=\!\!\! & C-NH_2 \\
| & & | \\
CO & & CH \\
| & & \| \\
NH & \!\!-\!\! & CH
\end{array}
\quad .H_2O.-$$
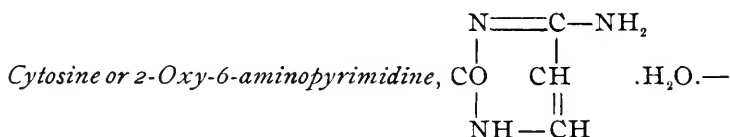
The above 2-ethylmercapto-6-aminopyrimidine (3 grams) was boiled with hydrobromic acid of boiling-point 125° (15 cc.) for two hours, when mercaptan had ceased being evolved. On evaporating the free hydrobromic acid on the steam-bath a beautiful crystalline mass of the hydrobromide was obtained. It crystallizes in the form of glistening prisms from a little water. The free base was obtained by dissolving the hydrobromide in water and precipitating with ammonia. The weight of the crude base was 1.9 grams, which is a yield of 79 per cent of the calculated. In another experiment 7.5 grams of 2-ethyl-mercapto-6-aminopyrimidine gave 5.6 grams of 2-oxy-6-aminopyrimidine, or 90 per cent of the calculated. The base for analysis was boiled with animal charcoal and crystallized from water. It was dried in the air and the water of crystallization determined by heating in an oven at 100° to 110°.

0.5166 gram substance lost 0.0727 gram on heating.

	Calculated for $C_4H_5ON_3.H_2O$.	Found.
H_2O	13.95	14.07

The analysis of the dried material gave the following results :

0.2188 gram substance gave 0.3498 gram CO_2 and 0.0835 gram H_2O.

0.0939 gram substance gave 31 cc. moist N at 25° and 773 mm. pressure.

	Calculated for $C_4H_5ON_3$.	Found.
C	43.25	43.60
H	4.50	4.25
N	37.84	37.72

Properties of 2-Oxy-6-aminopyrimidine.—The free base, when first obtained, crystallized from hot water in the form of needle-like prisms. It was then somewhat colored (pale brownish), and melted, or rather decomposed, at 320° to 325° with violent effervescence, first becoming dark-colored a little below 300°. After boiling in aqueous solution with animal charcoal it crystallized in the form of beautiful, colorless, transparent plates. The edge of one of these crystals, which perhaps was made up of a number of plates, measured three-quarters of an inch in length. The faces were so badly etched, or striated, or covered with vicinal growths, that crystallographic measurements were impossible. They probably belong to the mono- or triclinic system. The plates had the same effervescing-point on heating as the needle-like prisms. These decomposing-points were taken in capillary tubes, in a paraffin-bath, on an Anschütz thermometer 13.5 centimeters in length, and are uncorrected. The plates dissolve in about 129 parts of water at 25°. The base is precipitated by phosphotungstic acid. It would, therefore, be found in the histidine fraction. When the acidified solution is treated with potassium bismuth iodide it gives a brick-red precipitate. It gives the murexide reaction. With sulphuric and hydrochloric acids it gives readily soluble salts. The chloroplatinate, and especially the picrate, are difficultly soluble in water. The gold double salt is also not very soluble. Kossel and Steudel give

no melting- or decomposing-point for their cytosine, but state that the picrate turned brown on heating to 255° and melted at 270° with decomposition.

2-Oxy-6-aminopyrimidine Picrate.—Picric acid produced an immediate precipitate, which crystallized in bright-yellow needles or very slender, needle-like prisms. When made from material that had not been decolorized with animal charcoal, and therefore containing a slight impurity, it decomposed with violent effervescence quite sharply at about 264°. When prepared from the pure oxyaminopyrimidine the crystals had a more pronounced prismatic habit and they showed no melting-point, but sintered, became black, and decomposed at about 300° to 305°. One hundred parts of water dissolve 0.076 parts of the salt at 25°. Our experience with these picrates has shown that the melting-points are rather indefinite. They can be made to effervesce at a somewhat higher or lower temperature, according to the rate of heating. They are difficult to analyze on account of the ease with which oxides of nitrogen pass over. A nitrogen determination of a sample prepared from the pure base, for example, gave :

	Calculated for $C_4H_5ON_3.C_6H_2(NO_2)_3OH$.	Found.
N	24.7	26.4

The *chloroplatinate* separates as a precipitate in yellow flakes. A platinum determination gave :

	Calculated for $(C_4H_5ON_3)_2H_2PtCl_6$.	Found.
Pt	30.83	30.60

2-Oxy-6-acetaminopyrimidine was prepared by heating 0.5 gram of the amino derivative with acetic anhydride. It proved to be practically insoluble in alcohol and difficultly soluble in water. It crystallized from hot water in colorless, microscopic prisms, with rough faces, frequently occurring in crosses. It showed no signs of melting at 300°. A nitrogen determination gave :

	Calculated for $C_6H_7O_2N_3$.	Found.
N	27.44	27.82

The *phenyl isocyanate derivative* was prepared by heating 0.5 gram of the base with 0.55 gram of phenylisocyanate on the steam-bath for six hours. The white crystalline product which resulted proved to be very insoluble. It was boiled repeatedly with alcohol and then digested with water. The insoluble material thus obtained began to sinter on heating at about 255°, and then melted with violent effervescence at 260°. A nitrogen determination agreed with the calculated for an addition of 2 molecules of phenyl isocyanate to one of the base.

	Calculated for		Found.
	(1 : 1) $C_{11}H_{10}O_2N_4$.	(2 : 1) $C_{18}H_{15}O_3N_5$.	
N	24.34	20.05	20.4

Action of Bromine.—Three-tenths gram of 2-oxy-6-aminopyrimidine was treated with 1 gram of glacial acetic acid, and 0.5 gram of bromine was added. An immediate reaction took place, heat was evolved, and an orange powder separated, which dissolved on warming. Some water was added to the cooled solution and the precipitate produced was crystallized from water. It formed well-crystallized, colorless needles, and it melted sharply at 247° with effervescence. When dissolved in water and made alkaline with ammonia it gave a strong, wine-red color, and, on cooling, a brick-red substance separated. This had no definite melting-point.

$$
\begin{array}{ccc}
& \text{NH—CO} & \\
& | \quad\quad | & \\
\textit{2-Amino-6-oxypyrimidine, } \text{H}_2\text{N—C} & & \text{CH.—Thirty grams} \\
& \| \quad\quad \| & \\
& \text{N——CH} &
\end{array}
$$
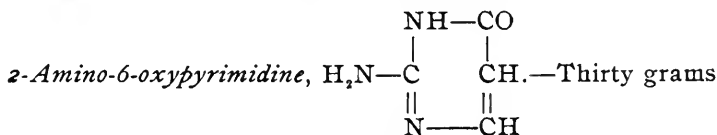
of guanidine carbonate were dissolved in 100 cc. of water and mixed with 54 grams of crystallized barium hydrate in 400 cc. of water. The solution was filtered and 55 grams of sodium ethyl formylacetate were added. The whole dissolved except a slight sediment. After standing for three hours the solution was divided into two equal portions. One was allowed to stand over night, the other was warmed on the steam-bath for a few minutes, and then just acidified with sulphuric acid. The filtered solution on evaporation, and adding ammonia in excess, gave a crystalline, brown precipitate, weigh-

ing 6.7 grams, or 36 per cent of the calculated. The portion
that stood over night, on similar treatment, gave practically
the same yield, so that long standing does not better the
yield. In another experiment 10 grams of guanidine carbon-
ate and 22 grams of sodium ethyl formylacetate gave 4.8
grams of the base, which is a yield of 39 per cent of the cal-
culated. On boiling the crude products with animal char-
coal, in aqueous solution, the color is slowly removed and, on
cooling, small, flat, colorless, transparent prisms generally
separate. These crystals, when air-dried, contained less than
0.5 per cent of water. A nitrogen determination (I.) gave :

I. 0.0900 gram substance gave 30.6 cc. of moist N at 26°.5
and 762 mm. pressure.

II. 0.1357 gram substance gave 44.8 cc. of moist N at 24°
and 768 mm. pressure.

	Calculated for $C_4H_5ON_3$.	Found. I.	II.
N	37.83	37.98	37.45

In another experiment, as above, the base was crystallized
from water, purified with animal charcoal, and when a por-
tion had separated from the still warm solution, in the form of
prisms, the mother-liquor was decanted. It then became al-
most semi-solid from the separation of a mass of long, slender,
colorless, silky needles which, on drying in the air, formed a
bulky, felt-like mass. This material contained, or occluded,
water, but the determinations were not constant : 0.8567 gram
substance lost 0.1036 gram on heating to 100° to 110°, equiva-
lent to 12.0 per cent water. The needle form appears to re-
sult also from dilute solutions or on rapidly cooling. 2.0527
grams of substance prepared in this manner, on standing in
the air for eight or nine hours and then heating, lost 0.1657
gram, equal to 8.7 per cent of water. The calculated for 1
molecule of water is 13.9 per cent. A nitrogen determination
of the dried material is given above (Analysis II.).

Properties of 2-Amino-6-oxypyrimidine.—It was found that
the needles gave the stout prisms and the prisms could be ob-
tained in needle form under slight changes in the crystalliza-
tion. The crystals were not suitable for crystallographic

measurements, the faces being highly etched, especially the end faces of the prisms. The material melts, or rather decomposes, with violent effervescence, at about 276°. This effervescing-point may vary several degrees, according to the rate of heating.

The base is precipitated by phosphotungstic acid. It is not precipitated by potassium bismuth iodide in hydrochloric acid solution, but it gives a brick-red precipitate in solutions of the base in sulphuric acid. It gives the murexide reaction. Its sulphate and hydrochloride are readily soluble in water and the former crystallizes in flat prisms. The picrate is very difficultly soluble and the gold and platinum double salts are also not very soluble. When heated with 20 per cent sulphuric acid for two hours, at 145° to 150°, a portion of the material is converted into uracil.

2-Amino-6-oxypyrimidine Picrate.—When picric acid is added to a hot solution of the base in water a mass of bright-yellow needles separate. If slowly cooled slender prisms are formed. On heating, the crystals become less transparent at about 180°, showing evidence of darkening at about 255°, and signs of melting at 270°. Between this point and 280° they generally effervesce. They dissolve in about 1200 to 1300 parts of water at 25°. A nitrogen determination gave :

	Calculated for $C_4H_5ON_3 \cdot C_6H_2(NO_2)_3OH.$	Found.
N	24.70	24.72

The *chloroplatinate* separates in the form of small yellow needles, which form acicular crystals or spikes on slowly cooling the hot solutions. On heating, it decomposes above 200°, becoming brown, but not melting below 286°. A platinum determination gave :

	Calculated for $(C_4H_5ON_3)_2H_2PtCl_6.$	Found.
$Pt(=194.8)$	30.83	30.56

The *gold chloride double salt*, which seems to be more soluble than the platinum double salt, forms bright-yellow, stout prisms, which easily form a supersaturated solution. A gold determination gave:

	Calculated for $C_4H_5ON_3.HCl.AuCl_3.$	Found.
$Au(=195.7)$	43.51	43.57

2-Acetamino-6-oxypyrimidine.—One-half gram of the base required about 7.5 grams of boiling acetic anhydride to effect solution. On cooling, a colorless mass of crystals separated, so bulky that the test-tube could be inverted without loss of the contents. This material crystallizes in bunches of minute mother-of-pearl scales from alcohol, and it melts at 247° to a clear liquid. A nitrogen determination gave:

	Calculated for $C_6H_7O_2N_3.$	Found.
N	27.45	27.69

2-Amino-5-brom-6-oxypyrimidine.—Three grams of the base were suspended in 20 cc. of glacial acetic acid, in which it is difficultly soluble, and 4.5 grams of bromine were dropped in. The action took place smoothly and an orange powder separated. It weighed 6.6 grams, while the calculated amount for a hydrobromide of 2-amino-5-brom-6-oxypyrimidine is 7.2 grams. The yield obtained was 83 per cent of the theoretical. This hydrobromic acid salt forms long, slender, needle-like prisms, when crystallized from water, and it melts at about 273° with strong effervescence. When the aqueous solution of this is treated with ammonia the brom-base separates as a compact, granular precipitate, insoluble in alcohol and extremely difficultly soluble in water. It crystallizes from strong acetic acid in radiating masses of pointed plates, and it melts with decomposition at about the same temperature as the hydrobromide or the bromine-free base. It has acid properties and it dissolves in strong ammonia, but separates again unaltered on boiling off the ammonia. A nitrogen determination gave:

	Calculated for $C_4H_4ON_3Br.$	Found.
N	22.10	22.13

CIV.—ON CYTOSINE OR 2-OXY-6-AMINOPYRIMI-DINE FROM TRITICO-NUCLEIC ACID.

By Henry L. Wheeler and Treat B. Johnson.

It has been shown by Osborne and Harris[1] that uracil can be obtained from the nucleic acid of the wheat embryo.[2] As we wished to compare our synthetic uracil with some of the natural we asked Dr. Osborne for a sample. Not having the pure substance at hand, he very kindly supplied us with 1.35 grams of material obtained by evaporating the mother-liquors from the crystallization of his uracil.

We found that the material, after crystallizing six times from water, gave a solution which, on slowly evaporating, deposited flat, needle-like crystals, about a centimeter in length. This material was obviously not uracil, and, at Dr. Osborne's suggestion, we then examined the material for cytosine. We found, in fact, that it consisted of a mixture of apparently about equal parts of uracil and cytosine.

When a solution of 3 grams of picric acid, dissolved in 200 cc. of hot water, was added to the 1.35 grams of material dissolved in 50 cc. of hot water and the mixture was allowed to stand for twelve hours, beautiful, long, silky, bright-yellow needles separated. The weight of the picrate obtained was 1.7 grams. The needles, which had every appearance of purity, melted with effervescence, as Kossel and Steudel[3] state in the case of thymus cytosine at about 270°, turning brown a number of degrees below this temperature.[4] We took exactly 1 gram of this picrate for the preparation of the free base. The picrate was treated with an excess of sulphuric acid and

---

[1] Ztschr. physiol. Chem., 36, 85; Annual Report for 1901 of the Connecticut Agricultural Experiment Station, page 408.

[2] Osborne and Campbell : J. Am. Chem. Soc., 22, 379.

[3] Ztschr. physiol. Chem., 37, 378 (1903).

[4] Owing to the ease with which this picrate gives off oxides of nitrogen, the analytical results came high both for carbon and nitrogen, so that the results were without value. In this connection it may be stated that a nitrogen determination gave 26.5 per cent nitrogen, while a precisely similar result was obtained in the case of the picrate from the synthetic base, namely 26.4 per cent nitrogen. The calculated for $C_4H_5ON_3.C_6H_2(NO_2)_3OH$ is 24.7 per cent nitrogen.

the picric acid was removed by shaking with ether. The sulphuric acid was mostly removed by barium hydrate, and, on concentrating and adding ammonia, colorless, well-crystallized, slender, needle-like prisms of the free base separated. The amount of this material was 0.1641 gram. This, after washing with water, was dried by standing in the air, on paper, for twelve hours. It then lost 0.0181 gram on heating to constant weight at 110° to 120°, equivalent to 11.30 per cent of water, while the calculated for $C_4H_5ON_3.H_2O$ is 13.9 per cent water.

This base melted with strong effervescence at about 323°, precisely like the synthetical 2-oxy-6-aminopyrimidine, and when a portion was mixed with the latter substance the melting- or effervescing-point was not lowered.

After determining the solubility in water (see below) the base was then converted into the chloroplatinate. A platinum determination gave:

0.0830 gram substance gave 0.0253 gram platinum.

	Calculated for $(C_4H_5ON_3)_2H_2PtCl_6$.	Found.
$Pt(=194.8)$	30.83	30.48

The remaining material was given to Professor S. L. Penfield for a crystallographic examination and comparison with the corresponding platinum double salt prepared from 2-oxy-6-aminopyrimidine. Kossel and Steudel[1] state, in regard to the platinum chloride double salts prepared by them, that '' Das Platindoppelsalz des Störcytosins zeigte nämlich fast durchweg doppelbrechende Zwillingsformen, welche in der Weise aneinander gelagert waren, dass die Auslöschungsrichtung in dem einen Krystall einen Winkel von 53° mit der Auslöschungsrichtung des anderen Krystalls bildete. Diese Winkel wurden beim Cytosin aus Herings-und Störtestikeln gleich befunden, beim Cytosin aus Thymusnucleinsäure haben wir bisher solche Zwillingsformen überhaupt nicht beobachtet.''

[1] Ztschr. physiol. Chem., **37**, 379 (1903).

*Crystallography of 2-Oxy-6-aminopyrimidine Chloroplatinate
(Synthetic Cytosine Chloroplatinate).*

The crystals submitted for study were thin plates and for
examination with the microscope they were embedded in oil,
and over them a cover glass was placed.
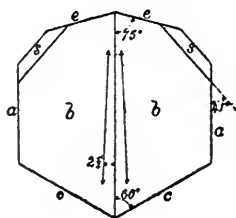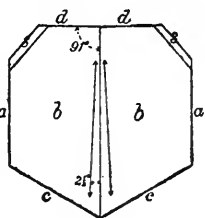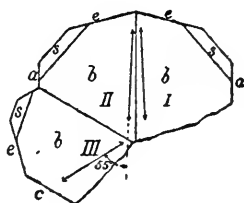
Fig. I.   Fig. II.   Fig. III.

Figure I. represents the habit of one of the crystals which
was unbroken and of almost ideal symmetry. It is a twin,
presumably belonging to the monoclinic system, the large flat
face *b* being the clinopinacoid (010). The edges *c*, *a*, and *e*
appear as sharp lines under the microscope, and represent the
direction of faces at right angles to *b*. It may be assumed
that *c* is the base (001) and *a* the orthopinacoid (100), the in-
clination of the axes, β, being about 60°. Some beveling
form, *s*, appears at the upper corners, which may be taken as
the monoclinic pyramid ($\bar{1}11$), its intersection with *b* making
an angle of about 41° with the vertical axis (the trace of *a*),
as indicated in the figure. The faces *e* at the top are ortho-
domes, inclined about 75° to the vertical axis, and they have
the symbol ($\bar{1}02$). The twinning plane, uniting the two in-
dividuals, is the orthopinacoid *a*. The extinction, indicated
in the figure by the arrows, is inclined about 2°.5 either side
of the twinning plane.

A second crystal, Fig. II., was like the one just described,
except for the faces *d* at the top, which make an angle of
about 91° with the vertical axis. The form *d* is evidently an
orthodome, and has the symbol ($\bar{1}03$).

A third crystal, Fig. III., showed two kinds of twinning.
Crystals I. and II. are twinned about the orthopinacoid as in

Fig. I., while II. and III. have the base *c* as the twinning
plane. The extinction is indicated by the arrows. In crys-
tals II. and III. the extinction directions make an angle of
55° with one another.

Crystallography of Wheat Cytosine Chloroplatinate.

The crystals submitted for study were much thinner than
those prepared from synthetic cytosine, hence when mounted
in oil for examination they were much more broken.
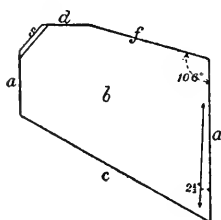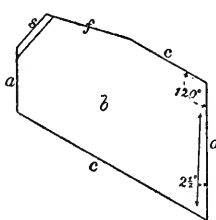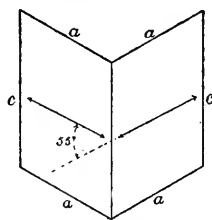
Fig. IV.   Fig. V.   Fig. VI.

Fig. IV. represents a fragment of a twin crystal, the part
to the right of the twinning plane not being shown. The ar-
rangement of the faces and the angles is like Fig. II., except
f, at the top, which makes an angle of 106° with the vertical

axis and corresponds to an orthodome ($\overline{1}$06).

Fig. V. represents a part of another twin crystal, like Fig.
IV., except that *f* and *c* terminate the crystal instead of *d* and
f. The extinction was 2°.5 from the vertical axis as in the
case of the synthetic preparation.

Among the broken fragments two kinds of twinning were
observed, some with *a* as the twinning plane and others like
Fig. VI., with the base *c* as the twinning plane. In the latter
the twinning law is the same as that of crystals II. and III. of
Fig. III. The extinction is nearly parallel to *a*, and makes
an angle with the twinning plane of 62°.5, or the two extinc-
tion directions make an angle of 55° with one another.

Aside from the extinction directions the optical properties
of the crystals were not very decisive. When examined in
convergent light an indistinct interference figure was seen,
presumably the center of the cross of an obtuse bisectrix.

The identity of the synthetic cytosine and wheat cytosine is established beyond question by the crystallographic similarity of the two chloroplatinates.

The measurements given were made under the microscope, and only approximate accuracy is claimed for them. The symbols of the domes e ($\bar{1}02$), d ($\bar{1}03$), and f ($\bar{1}06$) were determined by plotting.

Dr. P. A. Levene has very kindly sent us a pure sample of his base from the spleen which has the properties and composition of Kossel and Steudel's cytosine. The amount of this at our disposal was about 0.12 gram. It formed thin, flat, colorless crystals or prismatic plates, and it melted or effervesced, side by side with the synthetic material at 323°, and, when portions of these substances were mixed, the melting-point was not altered in the slightest. After determining the solubility we converted this material into the chloroplatinate. Professor Penfield then reported on the crystallography as follows :

Crystallography of Spleen Cytosine Chloroplatinate.

The crystals are like the ones previously described, having the same angles, though presenting some variation in habit. Fig. VII. is typical, showing *a*, *b*, *c*, and *s* forms, but with
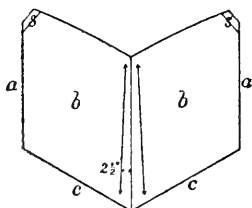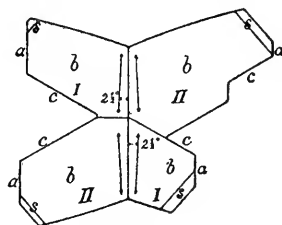
Fig. VII.   Fig. VIII.
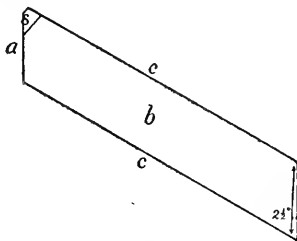
Fig. IX.

the reentrant angle at the top having a curved contour so that no definite symbol can be assigned. The extinction, as in the other preparations, is 2°.5 either side of the twinning plane, as indicated by the arrows in the figure.

Fig. VIII. represents a penetration twin, drawn with camera lucida. The two opposite parts I. and I. extinguish simultaneously, as also II. and II. Many crystals of the crop submitted for examination were long, lath-shaped individuals, Fig. IX. Several having this habit were twinned about the *c* face.

The three chloroplatinates prepared from synthetic cytosine, wheat cytosine, and spleen cytosine are crystallographically identical and show no greater variation in habit than is generally observed on crystals of any substance formed under varying conditions.

The solubility of the three samples of cytosine in water at 25° was determined with the following results :

100 parts water dissolve 0.83 part wheat cytosine.

100 parts water dissolve 0.78 part spleen cytosine.

100 parts water dissolve 0.79 part synthetic cytosine.

The high result in the case of wheat cytosine is probably due to the fact that it was not as pure as the others. Owing to lack of material the determination was made with the above-mentioned sample, which had been washed but not recrystallized from water.

We conclude, from these results, that the products obtained from the three different sources are identical, and that cytosine, is as Kossel and Steudel have predicted, an oxyaminopyrimidine, *viz.*, 2-oxy-6-aminopyrimidine. Its structure is to be represented by the following formula, or a tautomeric form :

$$\begin{array}{ccc} N \!\!=\!\!\!=\!\! C & -NH_2 \\ | & | \\ OC & CH \qquad .H_2O. \\ | & || \\ HN\!\!-\!\!-\!\!CH \end{array}$$
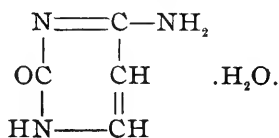
Hitherto cytosine has been found only in animal organs. The present results offer further evidence of the similarity of nucleic acids of animal and vegetable origin.

We take pleasure in thanking Dr. Osborne and Dr. Levene for the material placed at our disposal and Professor Penfield for the crystallographic descriptions.

IDENTIFICATION OF ORGANIC ACIDS BY THEIR TOLUIDES.

BY HEYWARD SCUDDER.

It is customary to make anilides and toluides by heating the base with the anhydride or chloride of the acid. When only a small amount of the acid is available it may be necessary to prepare as little as o.1 gram of the anhydride or chloride, a troublesome matter if the derivative is liquid, unless one is in the habit of handling small quantities.

The following modification of Petersen's[1] method of preparing amides from the sodium salt of the acid does away with the need of preparing an anhydride or chloride. The sodium salt need not be anhydrous, so that the time necessary for drying is not lost, and the reaction itself is moderately rapid. The time factor is of some importance in making derivatives for the purpose of identification, since under these conditions rapidity is more essential than getting a large yield, provided always that the yield obtained from a small amount of the acid is sufficient to be purified easily. *p*-Toluidine is chosen as the base because the *p*-toluides of most acids are solid, and there is usually a greater difference between the melting-points of the *p*-toluides of two adjacent acids in a series, *e. g.*, acetic and propionic, than between those of the isomeric toluides or of the anilides of the same acids.

Procedure.—Mix in a dry 6-inch test-tube 1 to 1.2 grams of *p*-toluidine and 0.3 to 0.4 cc. concentrated hydrochloric acid (sp. gr. 1.2). Add about 0.4 gram of the sodium salt of the acid. Support the test-tube in a clamp, resting the bottom of the tube in a hole 1 centimeter in diameter cut through a piece of asbestos felt. The asbestos prevents overheating the sides of the tube. Heat for one hour over a small flame. The

[1] Ann. Chem. (Liebig), **107,** 331 (1858).

height of the flame should be so regulated that the toluidine vapor condenses on the sides of the tube between one-third and one-half way from the bottom. If the sodium salt is anhydrous, the ring formed on the sides of the tube by the condensing toluidine will be distinct. But if the salt contains water of crystallization the water will condense all the way up to the top of the tube and the ring may not be clearly marked. In such a case it is advisable to remove the flame for a minute or two after heating for twenty minutes. When the heating is resumed the ring will be visible.

The toluide is best purified by crystallization from benzene or petroleum ether, in which a resin-like body that forms is very soluble. This resin can also be removed by boiling with water (which dissolves the toluide) and filtering hot, leaving the resin on the filter. In such a case it is usually best to boil the filter and resin in a few cubic centimeters of water and filter hot into the first filtrate, for the resin holds the toluide tenaciously, and keeps back a surprising amount, unless care is taken that the boiling is sufficiently prolonged to leave only a very thin layer of resin on the filter. The resin is readily soluble in alcohol. If the toluide is not white, a second crystallization is necessary.

The yield is good. In the case of acetic acid 0.4 gram of the sodium salt containing water of crystallization corresponds to about 0.2 gram of the acid. If one has had experience in handling small quantities it is possible to get sufficient of the toluide from 0.1 gram of the sodium salt. If less of the sodium salt is used than is called for in the preceding directions, the quantity of hydrochloric acid should be diminished correspondingly. But the quantity of *p*-toluidine should never be less than 0.5 gram, otherwise so little is left in the bottom of the tube when the mixture begins to boil that overheating occurs, and the proper reaction does not take place. An excess of hydrochloric acid must not be used.

This reaction has been tried on a number of acids and found to be generally available. Formic acid gives chiefly oxaltoluide instead of formtoluide.

If a volatile acid (as one of the lower fatty acids) is present

in solution, the proper weight of the salt can be obtained by distilling the acid into a solution of 0.12 to 0.14 gram of sodium hydroxide in 3 cc. of water colored by phenolphthalein, until the color has disappeared, and then boiling the solution down to dryness. The presence of moderate amounts of sodium chloride or sulphate do not influence the reaction.

In the case of most solid acids and acids of high boiling-point, it is not necessary to use the sodium salt, but 0.1 gram of the acid itself can be heated with the p-toluidine and hydrochloric acid as directed. The presence of the hydrochloric acid has a great effect on the rapidity of the reaction in some cases. Thus 0.1 gram of benzoic acid heated for one hour with 0.7 gram p-toluidine gave a very small yield of toluide. The same amounts of benzoic acid and toluidine, to which 0.1 cc. of concentrated hydrochloric acid had been added, gave a good yield when heated for only one-half hour. Oxalic acid and most acids that readily form anhydrides by the action of heat alone do not need the addition of hydrochloric acid.

The time required to get a sufficient yield of toluide varies greatly. One hour's heating has been found sufficient. But it is longer than is necessary in many cases. Oxalic acid gives an excellent yield when heated for only ten minutes. The experiments made with sodium oxalate were carried out with one hour's heating, but there is no reason to believe that this shorter period would not have been sufficient, for the organic acid is, of course, liberated when the mixture is heated.

Other salts, as barium, calcium, ammonium, etc., work quite as well as the sodium salts. Some toluides, *e.g.*, propiontoluide, are quite volatile at temperatures considerably below their melting-points, and cannot safely be dried at 100°.

Detailed directions for the best methods of rapid preparation of the anilides and toluides of a number of organic acids, as a means of identification, will soon be published by Dr. S. P. Mulliken, of this laboratory, in his "Method of Qualitative Organic Analysis."

MASSACHUSETTS INSTITUTE OF TECH-
NOLOGY, February, 1903.

REVIEWS.

EXERCISES IN QUALITATIVE CHEMISTRY, CHIEFLY INORGANIC. By JOHN WHITE, PH.D., Professor of General and Analytical Chemistry, University of Nebraska. New York : Henry Holt & Co. 1901.

Professor White's manual is intended (to quote the author's preface) '' to enable the student to complete for himself by purely inductive methods a fairly complete conception of analytical processes.'' For example, the student studies the reactions on barium, calcium, and strontium salts, respectively, of alkali oxalate, carbonate, dichromate, and phosphate. He is then asked to devise and test a method for detecting and separating these metals. The book is not intended to supplant the instructor. Indeed, its usefulness would depend on the criticism and explanations of the teacher. Professor White's book is simple, clear, and suggestive.

E. R.

A BRIEF COURSE IN QUALITATIVE CHEMICAL ANALYSIS FOR SCHOOLS AND COLLEGES. By JOHN B. GARVIN, B.S.(University of Illinois), Instructor in Chemistry in East Denver High School, Denver, Colorado. Boston : D. C. Heath & Co. 1902.

Mr. Garvin's manual is in the first part similar to that of Professor White, but while the latter is written for college students, Mr. Garvin's book is briefer and better adapted to the use of schools. The book consists of three parts : a study of bases, a study of acids, and a scheme for systematic qualitative analysis. It is well and carefully written.   E. R.

CHEMISTRY BY OBSERVATION, EXPERIMENT, AND INDUCTION. A Laboratory Manual for Students. By J. I. D. HINDS, PH.D., Professor of Chemistry in the University of Nashville. New York : John Wiley & Sons. 1902.

This is a simple laboratory manual to be used with the author's ''Inorganic Chemistry.''   E. R.

TEXT-BOOK OF ELECTROCHEMISTRY. By SVANTE ARRHENIUS, Professor at the University of Stockholm. Translated by JOHN MCCRAE, PH.D. London, New York, and Bombay : Longmans, Green & Co. 1902.

The English edition of the Electrochemistry by this celebrated man has recently appeared. The author states that the basis of the book is a series of lectures delivered at the University of Stockholm. The character of the work can be seen best from the contents. The subject is treated in seventeen chapters, having the following titles : Fundamental physical and chemical conceptions, older electrochemical views, the laws of Avogadro and van't Hoff, vapor-pressure

of solutions, boiling-point and freezing-point of solutions, general conditions of equilibrium, velocity of reactions, electrolytes, electrolytic dissociation, conductivity of electrolytes, degree of dissociation and dissociation constant, conclusions from the dissociation theory, additive properties of solutions, equilibrium between several electrolytes, calculation of electromotive forces, potential difference between two bodies, oxidation and reduction elements, secondary elements, electro-analysis, development of heat by the electric current.

The English translation is from the German translation of the original, which was in Swedish. The appearance of two translations so quickly after the original was published would indicate a large demand for the work.   H. C. J.

JAHRBUCH DER ELEKTROCHEMIE. Begründet und bis 1901 herausgegeben von W. NERNST, o. Professor an der Universität Göttingen, und W. BORCHERS, o.Professor an der Technischen Hochschule zu Aachen. Berichte über die Fortschritte des Jahres 1901. Herausgegeben von DR. HEINRICH DANNEEL, Privatdocent der physikalischen Chemie und der Elektrochemie an der Technischen Hochschule zu Aachen. VIII. Jahrgang. Verlag von Wilhelm Knapp, Halle a. S. 1902.

As will be seen from the above, the editorship of the Jahrbuch der Elektrochemie has been transferred from Nernst and Borchers to Danneel. He is, however, assisted by a number of co-workers, as Kenasy, Elbs, Harms, Kügelgen, and Mugdan.

The work appears, as formerly, under the two heads : Scientific Part and Applied Electrochemistry. The scientific part begins with a discussion of such general matters as laboratories, books on electrochemistry, general electrical apparatus, and new methods of work. The new contributions to the general theories of electrochemistry are then reviewed, and this is followed by reviews on conductivity of solutions, electrical energy, polarization, and electrolysis.

The applied electrochemistry begins with a review of the recent work on primary and secondary cells. This is followed by a review of the recent work on inorganic products produced by means of the electric current, including both metallic and metalloid elements, their carbides, and much more complex compounds such as sulphuric acid, perchlorides, etc.

The applications of electricity to organic chemistry, made in 1901, are then reviewed. These include the electrosynthesis of organic compounds, and the electrolytic reduction and oxidation of organic substances.

The reviews, on the whole, appear to be clear, comprehensive, and concise, and one can find here in a comparatively

short compass what would require very wide reading to obtain directly from the original articles. The work is undoubtedly well worth doing, and will contribute largely to the understanding and development of electrochemistry both pure and applied. H. C. J.

KURZE ANLEITUNG ZUR MAASSANALYSE MIT SPEZIELLER BERÜCKSICHTIGUNG DER VORSCHRIFTEN DES ARZNEIBUCHES. VON DR. LUDWIG MEDICUS. Siebente und achte, verbesserte und vermehrte Auflage. 1902. Tübingen : Verlag der H. Laupp'schen Buchhandlung.

The book deals with the elementary principles of volumetric analysis with special reference to the application of these principles to testing pharmaceutical products. General methods are given for the various processes involved in alkalimetric, acidimetric, iodometric, oxidation, and precipitation analyses. Under each chapter details are given for the testing of the various pharmaceutical products. No attempt is made to discuss any of the processes critically, and the worker is led to believe that each method will proceed as smoothly as it is represented on paper. It is questionable whether a book of this nature is at all useful to any other than the particular class for whom it is intended. The pharmacist would, however, be able to get from it a very clear statement of the facts in regard to volumetric analysis, and would in most cases be able to make satisfactory analyses of the products offered him.

In an appendix are given methods for the determination of carbon dioxide in air, the analysis of water, and the determination of the more important constituents of wine. That the book has been found useful is indicated by the number of editions through which it has passed. H. F.

PLATTNER'S MANUAL OF QUALITATIVE AND QUANTITATIVE ANALYSIS WITH THE BLOWPIPE. Translated from the sixth German edition by HENRY B. CORNWALL, A.M., PH.D., with the assistance of JOHN H. CASWELL, A.M. New York : D. Van Nostrand Company. 1902. pp. xvii + 463. Price, $4.50.

This book has long been recognized as one of the few standard works on analytical chemistry, and as such it is more or less familiar to every student of chemistry. This new and revised edition is thoroughly up-to-date. Many new minerals have been introduced, while tests and determinations of little value have been discarded. Spectroscopic methods have been omitted and modern chemical notation has been introduced. The book in its present form will be welcomed by the mineralogist, the chemist, and all who have to do with blowpipe analysis. F. H. G.

AMERICAN

CHEMICAL JOURNAL

THE REDUCING ENZYMES.

BY M-EMM. POZZI-ESCOT.

The reducing enzymes were discovered by J. de Rey-Pailhade, and he was the only one to occupy himself with this question up to the end of the year 1901, when, at his suggestion, I undertook the study. My first communication upon that subject to the Academy of Sciences of Paris bears the date January 6, 1902.[1]

For a long time the existence of reducing enzymes was denied. Their reality is above suspicion, and at the present time no one has any doubts about it. De Rey-Pailhade even believes—and he will pardon me for making public this unpublished part of his correspondence—that there are "reductases" and also "hydrogenases." I agree with him fully, but am inclined to believe that there is but one large family in which is a group of individuals whose reducing function is also to add hydrogen (hydrogenize). It is an idea somewhat difficult to explain, and since we lack definite facts to establish it, I shall simply mention it.

De Rey-Pailhade gave the name "philothion" to the en-

[1] M. Emm. Pozzi-Escot: "Contribution à l'étude du philothion," Compt. rend., **134**, 66 (1902).

zyme discovered by him. In 1885, in an investigation under-
taken to determine the mechanism of the elimination, in the
organism, of free sulphur taken into the gastro-intestinal
tract, he was led to the conclusion that there is direct com-
bination of this sulphur with nascent hydrogen of fermenta-
tion with the formation of hydrogen sulphide.[1] The next
year, 1886, he communicated to the Society of Natural His-
tory of Toulouse the result of experiments that led him to ad-
mit the existence, in living cells, of an organic substance that
could form hydrogen sulphide when in contact with free sul-
phur,[2] but this was only his personal conviction without posi-
tive proofs to support it. It was necessary to isolate this ac-
tive substance, to extract it from the cells containing it, to
show that it actually had the characteristics of an enzyme.
He made a large number of unsuccessful experiments before
reaching this result, but finally, in 1888, he showed that an
active substance may be extracted from beer yeast by means
of alcohol.[3]

Nature of Philothion.

Philothion, like all other enzymes, must be a molecular com-
plex possessing active affinities and charged with a relatively
large amount of chemical energy. Its essential characteristic is
to form hydrogen sulphide from free sulphur. De Rey-Pail-
hade has been led to regard it as a special hydrogenized

[1] J. de Rey-Pailhade : "Sur le formation de l'hydrogène sulfuré dans l'organisme
à la suite de l'ingestion de quelques médicaments ; Thèse pour le doctorat de méde-
cine, Montpellier, (1885)," Bull. Soc. Hist. Nat. Toulouse, May 8, 1885.

[2] J. de Rey-Pailhade : "Recherches expérimentales pour expliquer l'absorption
du soufre par la voie gastro-intestiuale, " Bull. Soc. d'Hist Nat. Toulouse, 1886, p.
116.

[3] J. de Rey-Pailhade : "Sur un corps d'origine organique hydrogèuant le soufre à
froid," Compt. rend., June 11, 1888; "Nouvelles recherches physiologiques sur la sub-
stance organique hydrogènant le soufre à froid," *Ibid.*, July 2, 1888; "Sur un nouveau
principe immédiat, le philothion, et sur sa propriété d'hydrogener le soufre," Bull.
Soc. Hist. Nat. Toulouse, July 4, 1888.

About the same time that de Rey-Pailhade made known philothion and its funda-
mental property, M. Olivier, of the Revue Générale de Sciences, announced as a
great novelty and an important physiological discovery, that the organic matter of
the " sulphuraires" (*Oscillaria, Ulothrix,* and *Beggiatoa*, spp.) yields hydrogen sul-
phide with free sulphur. It was June 11, 1888, that de Rey-Pailhade made known philo-
thion and its remarkable property. The note of Olivier is dated June 8, but it was
not published until June 18. The priority of de Rey-Pailhade is incontestible.
Compt. rend., June 11, 18, 25, July 2, 16, and Aug. 13, 1888.

compound of the formula RH_2. R is here a radical, of as yet unknown composition, to which 2 atoms of hydrogen are loosely joined in much the same way as the 2 atoms of hydrogen that differentiate indigo-blue from indigo-white.[1] This would explain the action of reagents towards philothion.

Take, for example, the action of the halogens. Chlorine, bromine, and iodine destroy philothion instantaneously, an action which is due, according to de Rey-Pailhade, to a sudden removal of the hydrogen, as indicated in the following theoretical equation :

$$RH_2 + Cl_2 = R + 2HCl.$$
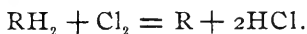
I do not wish to deny the explanation of de Rey-Pailhade, but may state that it is hypothetical, and he has never pretended to give it the value of a positive fact.

Preparation of an Active Hydrogenizing Liquid.

De Rey-Pailhade, at the beginning of my investigation, gave me the following method for the preparation of a solution of philothion. Treat 100 grams of cold, pressed top yeast with 55 grams of water and 45 grams of 90 per cent alcohol. Fill a bottle completely with the mixture, cork it, and shake for twenty-four hours at the ordinary temperature. Then filter, twice if necessary.

By following these directions one may, indeed, obtain a solution capable of hydrogenizing action, but I have found it necessary to modify the mode of operation in order to obtain more actively hydrogenizing solutions. At first I treated 1000 grams of the bottom yeast of beer, which is richer in reducing enzymes than top yeast, with 500 grams of 50 per cent alcohol, to which has been added a small quantity of an antiseptic, such as sodium fluoride, thymol, etc.

There are obtained much more active solutions by causing the plasmolysis of the dry yeast cells by means of some solid substance. De Rey-Pailhade uses sodium chloride,[2] but the

---

[1] This formula must be far from the truth. It seems to me much more logical to suppose that the hydrogen is not free, but is closely united to a radical, R, in somewhat the same way as the hydrogen of the aldehyde group.

[2] Congrès de Turin, Sept., 1901.

process that gives the best result is the following : Treat 500 grams of compressed yeast with 100 to 150 grams of powdered saccharose, and triturate the cooled mass. Soon the plasmolysis becomes quite active, producing complete liquefaction of the mass, which is then transferred to a precipitating vessel. A little thymol is added, and the whole is left for twelve hours. During this time the sucrase and zymase of the yeast act on the saccharose, causing exceedingly active fermentation with lively effervescence of the entire mass.[1] When the action is over, add a little water and filter. The solution is very active.

I have also obtained good results with pure glycerol. My experiments have shown that yeast that has developed in contact with the air is much poorer in the reducing enzyme than that which has led an anaerobic life. Hence bread yeast is much poorer than the bottom yeast of beer.

The liquid obtained by these different methods is slightly acid, a liter of it being equivalent to 1 to 3 grams of sulphuric acid. It is most active when in this condition. An exceedingly active solution may be obtained by precipitating the enzyme and redissolving it in a small quantity of water.[2]

General Properties of Philothion.

The active agent in the solution mentioned above was named philothion by de Rey-Pailhade.

The action of philothion upon oxygen[3] is especially impor-

---

[1] I have been asked for a proof of the existence of zymase. I find it in the fact that in the presence of an enormous excess of antiseptic, sufficient to kill every cell, the liquid obtained in the manner stated can change into alcohol as much sugar as the corresponding amount of yeast, and in a shorter time. It is well to state that this procedure permits the study of Buchner's zymase.

[2] It is difficult to precipitate the reductases by alcohol since it requires such an enormous quantity of the latter. I prefer ammonium or magnesium sulphate, or the method of Cohnheim or of Danilewski. See Pozzi-Escot : " Les diastases et leurs applications," pp. 58-59.

[3] J. de Rey-Pailhade : " L'oxidation de l'extrait alcoolique de levûre de bière," Bull. Soc. Hist. Nat. Toulouse, 27 Mars et Mai (1889) ; " Recherches expérimentales sur le philothion, principe immédiat répandu dans les deux règnes vivants, son rôle physiologique probable dans l'absorption de l'oxygène par la cellule vivante." Brochure in 8°, Mars (1891). Masson, editeur, Paris ; " Faits pour servir à l'histoire des oxydations intraorganiques, montrant l'absorption de l'oxygène," Bull. Soc. Hist. Nat. Toulouse, 7 Dec. (1892) ; "Nouvelles recherches sur le philothion, son rôle physiologique dans les oxydations intraorganiques, Congrès des Sociétés Savantes,

tant, and has caused much active discussion. Oxygen combines with philothion at the ordinary temperature, according to de Rey-Pailhade, who presents the following facts as sufficient proof for this statement : If an alcoholic solution of philothion, prepared as above, is exposed to the air, it loses its activity as an enzyme, after a certain time. On the other hand, if one performs a similar experiment with the same liquid, but removes the oxygen from the solution and the space above it by means of a current of pure hydrogen, nitrogen, or carbon dioxide, the extract retains its activity for a much longer time.

One may easily demonstrate the absorption and the hydrogenation of the oxygen dissolved in the extract of philothion by making a series of determinations of the dissolved oxygen by the method of Schützenberger.[1] The action of oxygen upon philothion may be represented thus :

$$RH_2 + O = R + H_2O.$$

R has the meaning given it in the formula of de Rey-Pailhade.

Philothion exists in most living cells, but the rôle played by oxygen in these organisms is known, so that one may well be surprised at finding philothion in them. Evidently, if the above-mentioned destruction is effective, and not a mere specu-

(1892)," Bull. Soc. Hist. Nat. Toulouse, p. 43 (1892) ; "Sur l'absorption de l'oxygène par les êtres vivants," Bull. Soc. Nat. Hist. Toulouse, 4 Mai (1893) ; " Mémoire sur l'absorption de l'oxygène par les tissus vivants, Congrès pour l'Avancement des Sciences, Besançon (1893)," Bull. Soc. Hist. Nat. Toulouse, p. 57 (1893) ; "Sur l'existence de deux ferments d'oxydation dans les plantes, Congrès pour l'Avancement des Sciences de Carthage (1896)," Compt. rend. soc. biol., 11 Mai (1896) ; "Sur l'oxydation des tissus," Bull. Soc. Hist. Nat. Toulouse, 2 Juin (1897); "Oxydations et réductions organiques," *Ibid.*, 7 Juillet (1897).

M-Emm. Pozzi-Escot : " Nouvelles recherches sur les principes réducteurs des tissus vivants," Compt. rend. de l'Académie de Médecine, 25 Mars (1902) ; "Principes réducteurs des tissus vivants," Soc. Médecine de Gand, 5 Juin (1902).

[1] The preceding facts were established by de Rey-Pailhade. I have shown that philothion, which must be a mixture of two reductases, is not always destroyed as rapidly as seems to be the case from his experiments. I have been able to keep in the laboratory, in a partly filled flask, a solution of philothion containing thymol from December 23 to the end of February. I must admit that it had then lost the property of hydrogenizing sulphur, but it still acted upon hydrogen peroxide, on indigo-carmine, and on tincture of guaiacum, all of which, as will be seen later, are characteristic reactions of a reductase. The facts seem to show that jacquemase is contained in philothion.

lation, there must occur simultaneously the destruction and regeneration of philothion.

The following is the explanation which is suggested by de Rey-Pailhade : When, in the organism, the philothion, RH_2, has been changed into R by combining with oxygen to form water, it returns to the condition RH_2 by the simultaneous action of R and of an oxidizable substance, R', upon a molecule of water. The water is dissociated, the hydrogen going to R to re-form RH_2, and the oxygen combines with the oxidizable substance, R' :

$$RH_2 + O = R + H_2O ;$$
$$R + H_2O + R' = RH_2 + R'O.$$
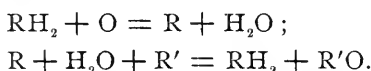
These equations represent a fact which must be regarded as certain until further information is obtained. We see, then, that philothion, together with water, acts as a carrier by means of which free oxygen is brought to the oxidizable substance. That is the part played by an enzyme, a chemical agent formed entirely by a living cell, and finally working for its benefit. (It is true that there are many enzymes that do not yet come under this definition, which, however, holds for certain groups of well-known diastatic ferments.) The quantity of oxygen absorbed in this indirect way appears to be important. The immediate regeneration of this principle by a phenomenon of hydrogenation is not only probable, but it is not without a parallel. It is known from the work of Armand Gautier that, in one part of the living cells of large animals the albuminoid tissues decay, when kept from the air, owing to the action of putrefying ferments. Thus the researches of Schloesing prove irrefutably that during the methane-fermentation of manure, water is decomposed into its elements. The oxygen combines with certain substances, and the hydrogen unites with carbon to form methane.[1]

---

[1] Schloesing (père et fils) : Ann. Agro., **18**, 5 (1893) ; Compt. rend., **109**, 835 (1889). Reiset: *Ibid.*, **108**, 708, 779 (1888). Deherain : Ann. Agro., **10**, 395. Gayon : Compt. rend., **98**, 528 (1884). Behrens : Centralbl. für Bakt., **3**, 584, 639, 783 (1897). It must be remembered that nothing absolutely definite is known of the methane-fermentation, although it is so common, and also very important, for to it is due the breaking-down of most of the cellulose produced each year on the earth's surface. An important chapter on this subject is contained in Duclaux's Traité de Microbiologie, **4**, 460.

We may approach the subject of the action of philothion upon oxygen in another way. It is known that indigo decomposes water, in the presence of a large number of oxidizable substances, in slightly alkaline solution. The indigo-white, in contact with oxygen, yields indigotin according to the equation :

$$2C_8H_6NOH + O = 2C_8H_5NO + H_2O.$$
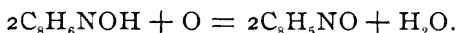
On the other hand, indigo-carmine, when in contact with water and ferrous oxide, acts according to the equation :

$$2C_8H_6NO + 2H_2O + 2Fe(OH)_2 = 2C_8H_6NOH + 2Fe(OH)_3.$$
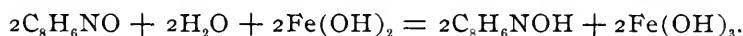
Comparing these two equations with those given above for philothion, we see that they are similar. Of course, the resemblance is only accidental, but it is not without value.[1]

I have taken up this theoretical part about the properties of philothion, and have obtained certain practical results of great interest that give a new idea of the rôle played by the reductases in the phenomena of oxidation taking place in the midst of living tissues (this work was brought before the Académie de Médecine of Paris by Armand Gautier, March 25, 1902).

I begin by preparing a very active solution of philothion and add to it 1 to 2 cc. of salicylic aldehyde, then the half-filled flask is closed with a ground-glass stopper and the mixture shaken, in contact with oxygen, for twelve hours. At the end of this time the liquid contains salicylic acid, which is detected as follows : The liquid is heated to boiling and the precipitated albuminoids are filtered off. Sodium carbonate is then added and the solution evaporated to dryness. The residue is dissolved in water containing hydrochloric acid and extracted with ether. The ethereal solution, when evaporated, yields crystals of salicylic acid, if any has been formed. This was the case in one experiment carried out in this way.

[1] De Rey-Pailhade: "Rôle du philothion et de la laccase en germination," Compt. rend., 121, 1162 (1885) ; "Sur l' existence simultanée, dans les tissus animaux, du philothion et de l'oxydase chargée de l'oxyder," Compt. rend. Soc. Biol., April 3 (1897); "Sur l'oxydation des tissus," Bull. Soc. Hist. Nat. Toulouse, 108, 3 (1897).

M-Emm. Pozzi-Escot : "Contribution à l'étude du philothion," Compt. rend., 134, 66 ; "Contribution à l'etude de la casse," Le Progrès Agr. et Vitic. de Moutpellier, March 9, 1902, p. 302.

In another series of experiments, I placed in contact with the hydrogenase some easily reduced substance containing oxygen, such as an iodate or arseniate, and found that the oxidation of salicylic aldehyde took place, apparently more actively. But too much value must not be attached to the determinations made under these conditions.

I do not pretend, as one might think, that philothion can act as an oxidase, but only that it may cause oxidation as a secondary reaction, accompanying the reduction, as the preceding experiments certainly prove. Hence, the theory of Hoppe-Seyler is verified.[1]

It may be noted that the above-mentioned oxidation may, perhaps, not be due to the fixation of oxygen, but to the loss of hydrogen, and, as A. Étard has shown, this is not because the oxidizing agents are strong or weak, but is due to combinations and decompositions depending on the relative structures of the oxidizing agent and the substance oxidized.[2]

This action of oxygen on philothion is of very great importance ; in the future it may play a leading part in our knowledge of the functions of the organism. We may say with de Rey-Pailhade that philothion, or more exactly, the reductases in the living cell are the gate, or one of the gates, through which free oxygen penetrates into the living cellular edifice. The tissues that use up much oxygen contain much philothion, or in other words, have a large gate for the entry of this indispensable aliment.

Reciprocal Action of Oxidases and Reductases.[3]

The reciprocal action of the oxidases and reductases is of

[1] M-Emm. Pozzi-Escot : "Les oxydases de la levûre," Revue Oenophile, 19, No. 4, p. 123 (1902), Bordeaux ; Armand Gautier : "Leçons de Chimie biologique," 2ᵉ Ed., p. 744.

[2] A. Étard : "De l'oxydation par voie de déshydrogénation au moyen des ferrocyanures : Oxydation du camphre," Compt. rend., 130, 569 (1900).

[3] De Rey-Pailhade : "Rôle du philothion et de la laccase dans les graiues en germination," Compt. rend., 121, 1162 (1895) ; "Sur l'existence simultanée dans les tissus vivant animaux du philothion et de l'oxydase chargée de l'oxyder," Compt. rend. Soc. Biol., April 30, 1897 ; "Sur l'oxydation des tissus," Bull. Soc. Hist. Nat. Toulouse, 108, 3 (1897).

M-Emm. Pozzi-Escot : "Contribution à l'étude du philothion," Compt. rend., 134, 66 ; "Contribution à l'étude de la casse, Le Progrés Agricole et Viticole de Moutpellier," March 9, 1902, p. 302 ; "Sur le commensalisme de certains ferments oxydants et réducteurs dans certains tubercules," Compt. rend., 134, 1006 (1902).

the greatest interest. Although we are not yet certain as to the mechanism of that action, we shall show what results have been arrived at. At first sight it seems as if the oxidases and reductases must be antagonistic, and experiment has shown that this is actually the case.

What should result from this antagonism where there are in the same cell, or in adjacent cells, secretions that oxidize, and others that reduce? It seems logical to admit that the labile elements of the two secretions will act reciprocally upon one another, there being a combustion of the hydrogen of the hydrogenase by the oxygen of the oxidase, and that this action will take place until one of the secretions is destroyed, leaving the field free for the action of the other. But these ideas are only *à priori*. It might be asked whether they are true, and especially whether they can be verified by experiment. De Rey-Pailhade has shown that when a tissue containing a reductase and an oxidase is finely ground, the oxidase seems to destroy the reductase by carrying the exterior oxygen, so that at the end of several hours only the oxidase is to be found, especially if the mixture be agitated in the air. Similarly, de Rey-Pailhade showed that the philothion in a germinating seed is often destroyed by the oxidase. According to his theory, the oxidases act on the hydrogenases, bringing about their destruction by combustion.

Admitting this to be true, it might still be asked whether the opposite might not be true also.[1] I have arrived at the following result : If, under suitable conditions, we allow a reductase to act on an oxidase, the reductase being in great excess, the oxidase may become "paralyzed" in its action. It is preferable to wait before penetrating the mechanism of this phenomenon, and giving a logical explanation of it.

De Rey-Pailhade has spoken of combustion ; this must be inexact. I am inclined to believe that there is a momentary combination of the two enzymes, and that the unstable compound thus formed—whose composition and nature escape us—by means of some new adhesive process fixes itself in insoluble form upon the solid substances with which it comes in contact, and is thus eliminated temporarily.

[1] M-Emm. Pozzi-Escot : Bull. soc. chim. de Paris, [3], **27**, 346 (1902).

The following is an unpublished experiment relating to this subject : The tubers of the dahlia (*Dahlia variabilis*), of the potato (*Solanum tuberosum*), and the Jerusalem artichoke (*Helianthus tuberosus*), contain oxidases. Sections of these tubers turn blue under the influence of an alcoholic tincture of gum guaiacum when exposed to the air. This reaction is of great interest and should be more closely studied. At first there is no change, then the blue is formed and disappears, and finally, at the end of a minute, the reaction suddenly acquires great intensity. This depends on the existence of oxidizing and reducing enzymes in the tubers. We may go still further in this way and cause solutions of a reductase and an oxidase to react upon one another. De Rey-Pailhade and I have accomplished this by experimenting in different ways. The experiment of de Rey-Pailhade follows : A solution of philothion is prepared by suspending compressed beer yeast in water containing 1.5 per cent of sodium fluoride. The mixture is put into a flask completely filled and stoppered. It is shaken for two days and then filtered. This antiseptic liquid yields much hydrogen sulphide when treated with powdered sulphur at 35°. The oxidase is obtained by grinding the cotyledons of germinating chick-peas for eight days in their weight of alcohol at 25°. This pulp is quite suitable for experiments. Two mixtures are made, each containing 25 cc. of the solution of philothion and 5 cc. of the pulp containing the oxidase. The first, A, is put into a flask of 150 cc. capacity, and the second, B, into a small bottle, which must be completely filled and well stoppered. A third mixture, C, made of 25 cc. of philothion and 5 cc. of oxidase which has been heated high enough to destroy this substance, is put into a 250 cc. flask.

The three flasks are mechanically shaken at the same time for five hours. When the liquid is then examined, it is found that A no longer contains philothion, although B and C contain a considerable quantity of it. The destruction of the philothion in the mixture C, where only the oxygen of the air acted, does not take place until after six or seven days, and it is found that the oxygen has almost entirely disappeared, and is replaced by carbon dioxide.

These experiments of de Rey-Pailhade seem to have established the following :[1] (1) That under the combined influence of the oxidase and oxygen, philothion is oxidized in a few hours ; (2) that by the action of oxidase alone, philothion is not destroyed; (3) that by the action of oxygen alone philothion is slowly oxidized.

Animal tissues always contain simultaneously both oxidase and philothion, so that, in contact with the air, the philothion is rapidly destroyed, and hence plays a greater or less part in the respiration of the tissues.

I have sought for the mechanism of these phenomena, and, as mentioned above, have studied the potato, commencing with an investigation of the oxidases contained in it. I have shown that, although spread throughout the tuber, they do not freely exercise their oxidizing action except in the part near the exterior, while at the center their influence is moderated by the influence of the reducing enzymes that also exist there. This has led me to the idea of the "commensalism" of the oxidizing and reducing ferments.

Abelous and Biarnès have also studied the oxidases of the potato, but without result.[2] They showed that the juice of potatoes, extracted by pressure and precipitated by alcohol, yields a precipitate which, when redissolved, cannot oxidize salicylic aldehyde, in either neutral, alkaline, or acid solution. They therefore conclude that "there is reason to believe that the laccase of certain plants does not oxidize salicylic aldehyde, and, consequently, the soluble ferment which causes the oxidation of salicylic aldehyde is not the same as the laccase studied by Bertrand."[3]

Potatoes contain oxidases and reductases, but, in the presence of air, that is, of oxygen, the oxidizing action preponderates, the reducing action being destroyed. This can be

[1] De Rey-Pailhade has really not shown that the destruction of the philothion was due solely to the action of the oxidase. Was it really an oxidizing enzyme that destroyed the philothion, and has the philothion really been destroyed?

[2] E. Barbier : Thèse de médecine, Toulouse, No. 122, p. 89, 1895-96. If these authors could not obtain any oxidizing action, it is because equilibrium was established between the oxidizing action of the oxidase and the opposite action of the reducing enzyme.

[3] "Contribution à l'étude des phénomènes oxydasiques dans les boissons fermentées," L'Oenophile, Feb., 1902, pp. 63-65.

shown as follows : Fill a long test-tube with bits of potato, and then pour upon them a dilute solution of indigo. Some of the upper pieces of potato are to be left uncovered by the liquid, and the whole is allowed to stand for twenty-four hours. It is then seen that the liquid is reduced at the bottom of the tube, is unchanged at the middle, and is oxidized at the part in contact with the air. The experiment is conclusive, but it does not always succeed.

The reciprocity of the action of the reductases and the oxidases has led me to suggest a new hypothesis regarding the disappearance of the oxidases of fruits during the alcoholic fermentation.[1]

In fruits and vegetable substances used in the fermenting vats, there exist oxidases localized in special cells, and hydrogenases also situated in distinct cellular elements. The existence of oxidases in fruits, and especially in the grape, is certain from the result of experiments by Martinand,[2] and of Bouffard and Sémichon.[3] It may be added that there are fruits that do not contain oxidases. The reductases also exist in fruits, as I have had occasion to show many times.

It follows that grape juice, before fermentation, generally contains enough oxidase to cause the ultimate breaking-down ('' la casse'') of the wine, yet it is known by experiment that a wine which has fermented normally is not generally subject to breaking down. All, or most of the oenoxidase of the original must is not found in the finished wine. Further, Alliot showed in 1901 that it is possible, by refermentation, to ameliorate and to render stable a wine that is apt to break down ('' cassable'').

By what means is the destruction of the oxidases, whose presence is so easy to show in the must, brought about, and why, in certain cases, does this destruction not take place ? Indeed, this has not been known. It seems as if people in the wine-growing districts have paid very little attention to it. The action of tannins has been suggested, and also the acidity, and this destruction has even been denied.

[1] Bouffard et Sémichon : Compt. rend., **126**, 423 (1898).

[2] See Progrès Agricole et Viticole, p. 553, 1901, and Feuille Vinicole de la Gironde, 1901.

[3] *Loc. cit.*

According to our hypothesis, the following must take place in the fermentation-vats : When the fruit is pressed and the cells crushed or destroyed, the enzymic elements which they contain diffuse through the liquid, come in contact, and mutually paralyze one another. What is the mechanism, then, that intervenes in order to eliminate the oxidase and the hydrogenase ? It is, in brief, a new force of adhesion that precipitates the mixture of enzymes. Whatever it may be, the external side of the phenomenon is evident.

What, then, is the origin of the reductase that comes into play ? It is double. There is at first that of the fruit and then that secreted by the yeast. De Rey-Pailhade has shown that yeast cells are exceedingly rich in hydrogenases. On the other hand, I have found that, contrary to the statements of van Laer,[1] living yeast, in full growth in an active solution, allows its hydrogenase to diffuse completely.[2] This diffusion takes place under certain conditions which I have determined in an investigation on the formation of hydrogen sulphide in alcoholic fermentations.[3]

Besides the destruction of the oxidase by the free hydrogenase, another phenomenon takes place, the rôle of which has not yet been definitely determined, though it is not very doubtful. There exists, in the must, free sulphur coming from the sulphur with which the vines are treated, in contact with which the hydrogenases yield hydrogen sulphide that destroys the oxidases.[4]

There remains to be explained the accidental presence of oxidases that finally cause the breaking-down of wine.

Finally, if the fermentation is bad, little hydrogenase is secreted by the yeast, the normal equilibrium is destroyed, and the conditions are reversed, as shown by de Rey-Pailhade.

Law of Reciprocal Action.

Different authors have shown that the above-mentioned

[1] Congrès des Brasseurs belges, Gand, July, 1901.

[2] "Les oxydases de la levûre," L'Oenophile, April, 1902, p. 121.

[3] M-Emm. Pozzi-Escot: "Mécanisme du formation de l'hydrogène sulfuré par fermentation alcoolique." Compt. rend., **134**, 628; Bull. soc. chim., **27**, 692 (1902).

[4] Some preliminary experiments have led me to believe that the oxydases are destroyed by alkaline sulphides and by hydrogen sulphide.

oxidizing enzymes extracted from potatoes do not oxidize salicylic aldehyde in acid, neutral, or alkaline solution. The reason for this has not been clear. It seems to me that this depends on a natural cause ; the existence in the tuber of two special classes of enzymic products that are mutually antagonistic, and whose action is governed by a law of equilibrium not well known. There is, on the one hand, a class of oxidases, and on the other, reductases analogous to jacquemase, which is secreted by *Eurotium Orizæ*. I have demonstrated the simultaneous existence of these oxidases and reductases. Kastle and Loevenhart[1] have, besides, proved the existence of the oxidases.

It was interesting to find out in which part of the potato these substances with contrary affinities were localized. This is what I investigated. I have shown, first, that if we apply directly the known reactions of oxidases to a slice of potato, it seems that the oxidases are localized in the cells near the periphery, but a more careful study of the phenomenon shows that in the deeper parts there is a state of equilibrium. I have, accordingly, applied to the tuber a method for the separation of the oxidases and reductases, based on the fact that, in a mixture of these two enzymes, the oxidases are more easily precipitated by absolute alcohol than the reductases. I have thus been able to show that all parts of the tuber are equally rich, apparently, in oxidizing enzymes. Why, then, do not all parts of the tuber have the same oxidizing power ? This depends simply on a state of equilibrium established between the oxidases and reductases. This state of equilibrium is seen perfectly in an experiment made by the method of Kastle and Loevenhart.

It seems, then, to be well established that there exists a perfect commensalism between the oxidases and reductases. Both are indispensable. The reductases seem to moderate the action of the oxidases. They hinder this as long as no exterior action destroys the equilibrium, and, as shown by Duclaux, we cannot separate the oxidizing from the reducing action, the oxidases from the deoxidases.

[1] This JOURNAL, **26**, 539 (1901).

Action of Philothion on the Metalloids of the Sulphur Family.

Philothion acts towards sulphur as a strong hydrogenizing agent. It is a most remarkable property that attracted the attention of de Rey-Pailhade and led him to the discovery of the hydrogenases. In his thesis for the degree of Doctor of Medicine, in 1885, de Rey-Pailhade showed that sulphur is hydrogenized when introduced into the organism, but his first communication on the mechanism of this action is dated June 11, 1888.[1]

Before him, Dumas[2] had established the fact that, when yeast is ground with sulphur and mixed with a solution of sugar in water, there is an evolution of hydrogen sulphide. At the same time that de Rey-Pailhade made this communication, L. Olivier,[3] of Pasteur's laboratory, showed that, contrary to the general belief, and the statements of Winogradski,[4] the organisms of glairin and baregin do not eliminate the sulphur which they contain in the form of sulphuric acid, but that they hydrogenize it. In this communication Olivier showed that, in these organisms, the sulphur plays a part analogous to that of oxygen, and that it is not oxidized by the cells. This is the theory that de Rey Pailhade was to devolop later in connection with the ferments of the organism.

I cannot do better than quote a typical passage from this memoir :[5] "These experiments suffice to prove that the organisms of baregin and glairin use up their intracellular sulphur without oxidizing it. They produce, at the expense of this metalloid, hydrogen sulphide and ammonium thiocyanate, a sulpho derivative of an isomer of urea. This fact, which is entirely new, seems to assign to sulphur a function of which no example has been known in physiology up to the present. Perhaps this substance can take the place of oxygen in the transformation of albuminoids into amido compounds, and, in a general way, in the combustion of living matter."

[1] J. de Rey-Pailhade : "Sur un corps d'origine organique hydrogénant le soufre à froid," Compt. rend., **106**, 1683 (1888).

[2] T. B. Dumas : Ann. chim. phys., [5], **3**, 92.

[3] Louis Olivier : " Experiences physiologiques sur les organismes de la glairine et de la barégine,—Rôle du soufre contenu dans leurs cellules," Compt. rend., **106**, 1744 (1888).

[4] Sergius Winogradski : Botanische Zeitung, **45**, 555 (1887).

[5] Compt. rend., **106**, 1745.

In a memoir published some time afterward, Olivier returns to this question, and shows clearly that the sulphuraires transform sulphur directly into hydrogen sulphide.[1] Olivier and de Rey-Pailhade worked entirely independently. It seems indisputable that the first suggestion of a hydrogenizing enzyme is due to the latter of these two men.

Olivier took into account only the intracellular sulphur,[2] and did not make a single attempt to isolate the hydrogenizing ferment which he suspected to be present. There is no doubt that de Rey-Pailhade had attempted this in 1886. In the next paragraph we shall see that the production of hydrogen sulphide by the reduction of sulphates has been known for a long time. The mechanism of the reaction may be established, *à priori*, by taking into consideration what we know of philothion and the experiments of Nastukoff.[3]

To show how easily sulphur is hydrogenized by the solution of philothion as prepared by de Rey-Pailhade, we may proceed as follows : Place some of the solution of philothion, prepared as above, into an Erlenmeyer flask with powdered sulphur or flowers of sulphur, and shake well. Then place over the mouth of the flask a piece of filter-paper saturated with subacetate of lead. Very soon we see that the part directly in contact with the interior atmosphere turns black from the formation of lead sulphide.

This hydrogenation in the cold is quite unique. It is only to be compared with the action of hydriodic acid on sulphuric acid.[4] It is easy to determine the quantity of hydrogen sulphide formed by the action of a given volume of the alcoholic extract of yeast upon sulphur. The extract of yeast and the sulphur are placed together in a small flask connected with a series of Durand wash-bottles containing a measured quantity of iodine solution of known strength. By means of an aspira-

[1] Louis Olivier : " Nouvelles experiences physiologiques sur le rôle du soufre chez les sulfuraires," Compt. rend., 106, 1806 (1888).

[2] Ann. de l'Institute Pasteur, 1897.

[3] Duclaux : " Traité de microbiologie," Vol. III., p. 179. Nastukoff, " Essai sur le pouvoir réducteur des levûres pures—Moyen de le mesurer," Compt. rend., 121, 535 (1895), admits that the sulphates are reduced during alcoholic fermentation. This is denied by Kulisch: Weinbau und Weinhandel, (1894). H. Quantin has proved that copper sulphate can be reduced during the fermentation (Compt. reud., 103, 888).

[4] Berthelot : Bull. soc. chim., 31, 310.

tor, a current of air or carbon dioxide is drawn through in order to carry over the hydrogen sulphide that is formed. The amount of iodine not reduced by the hydrogen sulphide is determined by a solution of sodium thiosulphate. From this we can deduce the volume or the weight of the hydrogen sulphide.

Naturally the amount of hydrogen sulphide produced depends on a number of circumstances. I have obtained very variable figures, and much more variable ones than those given by de Rey-Pailhade. He found that 100 cc. of the active liquid gave more than 1 cc. of hydrogen sulphide. In an experiment published elsewhere, I found 10 cc. De Rey-Pailhade does not state the duration of his observations. The temperature also plays an important part, for philothion, like all other enzymes, has its optimum temperature.

I have shown in a series of investigations that metalloids related to sulphur—selenium, tellurium, arsenic, and phosphorus—are also capable of being hydrogenized.[1] The hydrogenation of phosphorus in the organism has been announced before by Noé. I do not know what his results are.

Of these experiments I shall only state what has been done to show the addition of hydrogen to selenium. A mixture of 800 cc. of the very active hydrogenizing liquid, containing a large excess of antiseptic (sodium fluoride), and 2 grams of selenium was put into a large Erlenmeyer flask, which was closed with a rubber stopper. It was connected with a series of Durand wash-bottles containing caustic soda. The flask was kept for forty-eight hours in a water-bath heated to about 25°. At the end of this time the gas in the flask is driven over through the wash-bottles by means of a stream of carbon dioxide. Then the liquid in the flask is gradually heated to boiling, the current of carbon dioxide being continued. At the end of the experiment the presence of selenium is sought for in the first wash-bottle by microchemical methods,[2] the results showing that hydrogen has been added to the selenium. Besides, the odor of the gas in the flask was sufficiently characteristic.

[1] M-Emm. Pozzi-Escot : "Contribution à l'étude du philothion," Compt. rend., **134,** 66 ; Bull. soc. chim., [3], **127,** 346 ; Bull. Soc. Hist. Nat. Toulouse, p. 42, Feb. 5 (1902).
[2] M-Emm. Pozzi-Escot : " Analyse microchimique et spectroscopique," p. 78.

Reducing Action of the Reductases.

These reducing reactions are very interesting, and it was by a consideration of similar ones that I discovered jacquemase. Indigo-carmine is decolorized by philothion, and the same is true of an alcoholic tincture of litmus. It requires about fifteen hours, at the ordinary temperature, and even less at $35°$, to destroy a slight coloration of indigo-carmine. It must be a reduction, for the decolorized liquid, when shaken in contact with the air, at once regains its original blue color. A half liter of the extract easily reduced o.5 gram of indigo-carmine in a few hours. With the help of an intermediary substance the reaction can be carried out much more rapidly. A few grams of sulphur are put into a small flask, which is then filled with fresh extract, colored with indigo-carmine, corked, and shaken. The blue tint disappears after a few minutes, but returns as soon as the flask is opened. The phenomenon is easily explained: The indigo-blue, $C_{16}H_{10}N_2O_2$, is changed by the influence of the reducing agents into indigo-white, $C_{16}H_{12}N_2O_2$, which contains two more atoms of hydrogen ; thus, the philothion and the sulphur yield hydrogen sulphide which, under the influence of the indigo-blue, loses hydrogen with the simultaneous formation of indigo-white (colorless). There is, at the same time, a deposition of sulphur. But indigo-white is a substance very easily oxidized, even if it remains under the liquid.[1]

Action of Alkalies.

What precedes has to do with the natural extract, which is slightly acid. De Rey-Pailhade has studied the influence of alkalies. The alcoholic extract, when made alkaline by caustic soda, absorbs free oxygen and rapidly reduces indigo-carmine. The effect is the same with sodium carbonate. The alkaline extract, exposed to the air, loses in a short time its property of producing hydrogen sulphide in contact with free sulphur. Hence, the effect of alkalies is to render the philothion much more sensitive to the action of free oxygen.

[1] Nietzki : "Chimie des matières colorantes organiques," p. 369 (1901).

Action upon the Tincture of Gum Guaiacum.

The reductases act upon tincture of guaiacum, and this action is important.   It was the subject of a memoir presented by me before the Academy of Sciences.[1]   It has been known for a long time that the oxidases directly turn to a blue color the white emulsion obtained by putting a few drops of an alcoholic tincture of gum guaiacum into water,[2] and that other enzymes cause the same transformation when a few drops of hydrogen peroxide are added to the solution.   It had also been noticed that certain substances containing known enzymes, for instance, koji, which contains amylase, do not give any coloration under these conditions, and hence, at first sight they seem not to contain an enzyme, although they decompose hydrogen peroxide.   Several hypotheses have been suggested to explain this phenomenon, but they are not at all probable.

I showed, as soon as this fact became known, that it was due to the intervention of a new kind of enzyme possessing the property of reducing tincture of guaiacum.[3]   We can readily prove this by showing that an extract of yeast, prepared with saccharose, which is very rich in zymase and sucrase, as well as in philothion, does not act on the emulsion of gum guaiacum tincture, even in the presence of hydrogen peroxide, but on introducing a small quantity of philothion into a solution of guaiacum blue, which has been prepared beforehand by means of some mineral or enzymic oxidizer, the guaiacum blue is at once reduced.

These facts are of great importance, for they establish clearly that the reductases cannot be detected by a color reaction with tincture of gum guaiacum, and, on the other hand, that in a mixture of enzymes the tincture of gum guaiacum does not give any indication if reductases are present.[4]

From these facts it follows that a certain number of pub-

[1] M-Emm. Pozzi-Escot : " Sur une importante cause d'erreur dans la recherche des diastases," Compt. rend., **134**, 401.

[2] Bertrand : Bull. soc. chim., [3], **11**, 717 (1894).

[3] A detailed explanation of the phenomenon has been published in a memoir addressed by me to the Academy of Sciences. Compt. reud., **134**, 81 (1902) ; Bull. soc. chim., [3], **27**, 280 (1902).

[4] M-Emm. Pozzi-Escot : Ann. et Rev; de chim. analyt., **7**, 185.

lished researches on the enzymes and their localization in special cells, lose their value when we consider that these facts were established by means of colored reagents, upon which all the reductases acted, and that did not take this action into account ; and, too, these reductases are very abundant in living things.[1]

Action upon Certain Salts Containing Oxygen.

De Rey-Pailhade succeeded in reducing the arsenates to arsenites,[2] and Rabuteau reduced the iodates and bromates to iodides and bromides, respectively.[3] After verifying the work of these authors, I tried to cause the reduction of the nitrates, thinking that this, if successful, would have an interesting bearing upon the mechanism of the assimilation of these salts by plants. We know that, with few exceptions, plants produce their own proteids from mineral nitrogen. Although this has been known for a long time, we do not know through what successive phases or steps ammonia and nitrates pass before being transformed into albuminoid substances, and the mode of formation of the first stage of this transformation, and the nature of the substance which it represents, are still under discussion. It must be remembered that the nitrates enter the plant much dissociated on account of their extreme dilution, and, also, the slight acidity of the plant juices. That is, they are in a particularly unstable condition, the ionic state, which no doubt facilitates the exercise of chemical affinities. Armand Gautier thinks that the nitrates are reduced by the aldehydes in the leaves, according to the equations

$$HNO_3 + C_2H_6O = HNO_2 + C_2H_4O + H_2O$$
and $$HNO_3 + CH_3CHO = CHN + CH_2O_2 + H_2O,$$
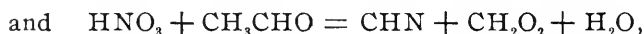
or by some similar reaction.[4] Bach believes that nitric acid is changed by reduction into hydroxylamine.[5]

Schloesing has given an explanation of a different order.[6]

[1] M-Emm. Pozzi-Escot : Compt. rend., **134,** 479.

[2] Rey-Pailhade : Congrès de Physiologie de Turin, Sept., 1901.

[3] Rabuteau : Traité de Thérapeutique.

[4] Armand Gautier : Leçons de Chimie biologique, Ed. 2, p. 36.

[5] Bach : Compt. rend., **122,** 1499.

[6] Schloesing fils: Compt. rend., **131,** 716 ; Ann. Agron., **28,** 144.

The existence of reducing enzymes in living cells, and particularly in growing plants, in the embryo buds at the extremities of the shoots, and in all parts where intercalary growth is not finished (which is just where the nitrates[1] are found) led me to see in the reductases the long-sought reducing agent.

From the coexistence of reductases and nitrates in the same parts of plants, we cannot help drawing conclusions favorable, *à priori*, to this view. In order to determine the exact relation between the nitrates and the reductases, I tried to bring about the reduction of nitrates by means of the reducing secretions of the cells. An active solution of philothion was prepared by one of the methods already given, and the following experiments were made with it :

	Solution of reductase. cc.	Potassium nitrate. Gram.
1	100	0.01
2	100	0.05
3	100	0.10
4	100	0.50
5	100	1.00

At first the reaction of the liquid was slightly acid, indifferent to metaphenylenediamine sulphate, to mercury potassium iodide, and to Trommsdorff's reagent. It did not contain a trace of cyanide.

Each experiment was enclosed in a flask with a ground-glass stopper. At the end of three days the experiment was ended, and the amount of unchanged nitrate determined, as well as the reaction of the liquid. Nos. 4 and 5 were the same as at the start, which is explained by the toxic action of the nitrates upon the hydrogenases, as I have shown elsewhere.[2]

Nos. 1, 2, and 3 were carefully examined. No. 1 gave freely the reaction for nitrites with metaphenylenediamine and

---

[1] P. Mazé : " Évolution du carbon et de l'azote dans le monde vivant," p. 84 (Bibliothéque scientifique. Carré et Naud).

[2] M-Emm. Pozzi-Escot : "Mémoire sur les actions catalytiques des hydrogénases," Compt. rend., **134,** 81 ; Bull. soc. chim., [3], **27,** 284.

It may be added that, in this experiment as in all other similar ones made by me, it has always been shown that a specimen of the diastatic liquid, kept for five minutes at 80° to 90°, remains inactive (neutral) indefinitely.

with Trommsdorff's reagent, and even a slight coloration with mercury potassium iodide. The nitrogen of the nitrate was determined after the destruction of the products of reduction. There was found 0.0041 gram, corresponding to a destruction of 0.0059 gram. When examined in the same way, Nos. 2 and 3 also gave freely the reaction with metaphenylenediamine and with the iodide, and showed, on examination, that some of the nitrogen of the nitrate had disappeared. Must we attribute the observed reduction to the hydrogenizing enzyme ? It is not certain, but it seems very probable. When taken in connection with the reduction of the iodates, bromates, and arsenates observed by de Rey-Pailhade, we can be almost sure of it. I wished to carry these experiments still farther, and, in place of extracting the enzyme in order to make it act on the nitrate, I wished to see if it were not possible to obtain a considerable reduction in a cell rich in hydrogenizing enzymes (reductases). For this purpose I used beer yeast that had been selected from the ordinary bottom yeast of the brewery, and grown in a pure culture for some time. This was put into a solution of pure saccharose, which was acidified with nitric acid and contained a suitable quantity of LaClaire's nutrient salts.

The experiments were carried out in Pasteur flasks containing 1 liter of syrup (80 grams of sugar to the liter), slightly acidified with nitric acid, and containing increasing amounts of potassium nitrate as the nitrogenous food, together with 1 gram of the phosphate of the same base.

Of the experiments which were made I will give only two :

(1) With 4 grams of potassium nitrate, inoculated Jan. 26.

(2) With 10 grams of potassium nitrate, inoculated Jan. 26.

The fermentation was slow in both flasks. It was hastened by shaking vigorously several times a day at first. The experiment was ended March 15. The yeast was isolated and dried rapidly on filter-paper, and the liquid in the flasks was tested with metaphenylenediamine and mercury potassium iodide. The liquid from flask (1) gave a slight coloration with phenylenediamine sulphate. The liquid in (2) did not react with this substance. Both flasks contained traces of sal

ammoniac. Considering only the liquid in the two flasks, we see that there was a reduction, but in only one case was there found nitrous acid, the intermediate stage.

Nitrates, nitrites, and ammonium salts were then looked for in the yeast cells. After drying the yeast, plasmolysis was brought about by the method already mentioned. In both cases it was shown that the cells contained nitrates, nitrites, and ammonium salts. These experiments seem very conclusive in favor of the reduction of nitrates in plants, although the reducing action of the sugars present is one great objection. In the case considered, which is the reducing agent, the enzyme or the sugar? The enzyme, it seems to me, but it cannot yet be stated positively.[1]

Abelous and Gérard found that aqueous extracts, containing chloroform, of certain organs change alkaline nitrates into nitrites.[2] I did not know of the work of these authors until quite recently, after having made my experiments and written what precedes. If we make a maceration of 40 grams of ground horse kidney in 100 cc. of water, and add 8 grams of potassium nitrate, and some chloroform to prevent the action

[1] I have recently undertaken new experiments, working with the young buds of trees. (" Étude sur le mécanisme de la réduction des nitrates chez les végétaux ; intervention d'une action diastasique," Compt. rend., **134**, 863.) I have thus been able to show clearly that there is really a reduction of nitrates under the influence of reducing enzymes. In the phenomenon of assimilation their intervention is undeniable. Experiments along this line were recently made with stems of burdock gathered at different times of the day. They were ground in a Simon grinder, then in a mortar, and finally squeezed in a press. The liquid was set aside. The cake was put into water, washed, and pressed, and the new liquid put with the first. An excess of ammonium fluoride was added and the whole divided into three equal parts, A, B, and C. A was let alone. B was heated to 85° to 90° for five minutes. To C was added nitrate of potassium. The three were left in a water-bath heated to 25° for fifteen to eighteen hours, at the end of which time it was found that a part of the nitrates existing naturally in A had been reduced to nitrites and ammonia derivatives decomposable by boiling with caustic soda. In C the action had been the same. In B the liquid remained as it was at first. In A and in C the ammonia was determined by treatment with caustic soda, figures much higher than for B being found. There had been, then, reduction and diastatic assimilation. These experiments have shown that the enzymes that reduce nitrates are very abundant, at the end of warm days, in actively growing plants, but that there is very little for some hours after sunrise, and after a cool night. From my experiments I believe that there is a difference between philothion, jacquemase, and the enzyme that causes the reduction of nitrates. I suggest for this the name of jacquemase β, jacquemase α being the first one discovered by me.

[2] Abelous et Gérard : "Sur la présence dans l'organisme animal d'un ferment soluble réduisant les nitrates," Compt. rend., **129**, 56.

of micro-organisms, we find that, after being warmed to 40°
for twelve to fifteen hours, the filtrate shows that the nitrate
has been reduced. If we work in the same way with ground
kidney, which has previously been heated to 100°, there is
no reduction. If we examine, under the same conditions, the
reducing power of the different organs of the horse, it will be
found that most of them reduce potassium nitrate, though not
all to the same extent. The precautions taken by these au-
thors do not allow us to attribute the reactions considered to
the intervention of parasitic micro-organisms. Finally, from
the systematic way in which they studied the influence of tem-
perature upon the progress of the reduction, there seems to be
no doubt that in this case the action is due to enzymes.

Abelous and Gérard afterwards made a comparative study
of the reducing power of different tissues. The following is
quoted to show their method of work :

" 1. Two hundred and fifty grams of ground kidney are
macerated in 300 cc. of distilled water, with the addition of
chloroform, for twenty-four hours at 42°, and then filtered.

"(*a*) To 100 cc. of the limpid filtrate are added 8 grams of
potassium nitrate and 1 cc. of chloroform.

"(*b*) One hundred cc. of the filtrate are heated to boiling,
then 8 grams of potassium nitrate and 1 cc. of chloroform are
added.

" After allowing them to stand four hours in an air-bath at
40°, the presence of nitrites is tested for by means of zinc
iodide, starch, and acetic acid (Tromsdorff's reagent). It is
found that (*a*) gives a decided reaction, while (*b*) gives none.

" The mixtures are left twelve hours longer, at the end of
which time (*b*) gives no reaction, while with (*a*) the reaction
is more decided than before. Hence an aqueous maceration
of horse kidney is capable of reducing nitrates. The temper-
ature of 100° destroys this property." [1]

They have also shown that the ferment[2] of this reduction is
soluble in glycerin. These experiments confirm what has
preceded.

[1] Abelous and Gérard. "Sur la presence dans l'organisme animal d'un ferment sol-
uble réducteur—Pouvoir réducteur des extracts d'organes." Compt. rend., **129**, 164.
[2] I revive here the word " ferment " which should be understood as " chemical
agent "

Abelous and Gérard published a second note,[1] which, I be-
lieve, should be sharply criticized. They admit that the re-
duction of the nitrates into nitrites is counterbalanced, in the
living tissues, by the opposite action brought about by the
intervention of the oxidases. In my opinion, this is self-con-
tradictory, and is entirely wrong, for it is impossible not to
see in the reduction of nitrates to nitrites the first stage of a
complex mechanism, known in ordinary language by the
name assimilation.

The Hydrogenation of Nitrobenzene.

Letheby[2] stated that nitrobenzene is reduced and trans-
formed into aniline in the body. Abelous and Gérard,[3] in re-
peating this work, were led to interesting results. They ex-
tracted from horse kidney a reducing enzyme, and showed its
action upon nitrobenzene. Ground horse kidney is macera-
ted with its own weight of distilled water for twenty-four
hours at 42°, in an atmosphere of hydrogen, some chloroform
being added. It is then filtered.

(*a*) To 100 cc. of the limpid filtrate are added 40 drops of
nitrobenzene and 2 cc. of chloroform, and the whole is then
enclosed in an atmosphere of hydrogen.

(*b*) To 100 cc. of the same filtrate, brought to boiling, are
added the same quantities of nitrobenzene and chloroform in
a flask filled with hydrogen.

The two flasks, inverted under water, are placed for forty-
eight hours in an air-bath heated to 42°. At the end of this
time each is shaken with ether. The latter is then decanted,
evaporated, and the residue tested for aniline by treating it
with a solution of calcium hypochlorite. With (*a*) there is
obtained a fine bluish-violet coloration, passing gradually into
red. On the contrary, (*b*) gives no color.

Hence, a clear, aqueous extract of horse kidney, containing
chloroform, is able to transform nitrobenzene into anil-

---

[1] Abelous et Gérard: "Sur la coexistence d'une diastase réductrice et d'une
diastase oxydante dans les organs animaux," Compt. rend., **139**, 1023.

[2] Würtz, "Dictionnaire," 1ᵉʳ Supp., Vol. I., p. 284.

[3] Abelous et Gérard: "Transformation de la nitrobenzine en phénylamine par un
ferment réducteur et hydrogénante de l'organisme," Compt. rend., **130**, 420 (1900).

ine by deoxidation and hydrogenation, according to the following equation :

$$C_6H_5NO_2 + 3H_2 = 2H_2O + C_6H_5NH_2.$$
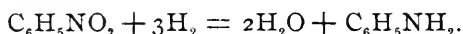
The reaction is due to the action of an enzyme, as shown by the influence of heat. Although Abelous and Gérard knew about philothion, discovered previously by de Rey-Pailhade in the kidney of the horse, they did not mention this hydrogenizing ferment in their memoir, and did not think of attributing to its action the new phenomena which they made known. De Rey-Pailhade replied to this injustice by a brochure, "Le philothion ou hydrogénase,"[1] in which he tried to establish by thermochemical considerations that philothion is able to cause the hydrogenation of nitrobenzene. I have tried to verify the fact directly by experiment.

Using a solution of philothion, I repeated the experiments of Abelous and Gérard, and obtained the complete reduction of nitrobenzene. It is an easy experiment to carry out. Five hundred grams of compressed yeast are treated with a convenient plasmolyzing agent, a sufficient amount of ammonium fluoride is added, and then a few cubic centimeters of nitrobenzene. The whole is then placed in a flask in a water-bath at $35°$. At the end of forty-eight hours it is treated with ether. The ether is decanted, evaporated on the water-bath, and aniline is tested for by the usual reagents, especially that of Jacquemin. There seems, then, to be complete identity between the ferment of Abelous and Gérard and philothion. I might remark besides, that there is no doubt about the true nature of the ferment discovered by Abelous and Gérard, and on the presentation of one of my notes to the Academy of Medicine, Armand Gautier identified it with philothion.[2]

Reduction of Sulphates.

It seems certain, at the present time, that sulphates are reduced during fermentation, as was shown by Quantin in connection with sulphate of copper,[3] and Nastukoff showed the

---

[1] "Le philothion ou hydrogénase : Considerations sur les experiences de MM. Abelous et Gérard," Toulouse (1900).

[2] Armand Gautier : Bull. Acad. Med., [3], **47**, 400 (1902).

[3] H. Quantin : "Sur la réduction du sulfate de cuivre pendant la fermentation du vin," Compt. rend., **103**, 888.

same for sulphate of magnesium.[1] Finally, it appears from different authors that the reducing agent is philothion, or a closely related reducing enzyme. It has been shown that in industrial fermentations there is very often a formation of hydrogen sulphide, even in a pure fermentation.[2] It is due to the reduction of the sulphates existing in the must, and is evidently caused by an enzyme.

Another fact which seems to speak in favor of the reduction of sulphates by reductases has been studied by Olivier;[3] that is, the production of hydrogen sulphide by sulphuraires.[4] It was shown long ago that there always exist bacterial organisms in all sulphur springs.[5]

These organisms are of especial interest, for nearly all of their cells enclose granules of sulphur. This shows that they exercise a certain influence upon the composition of the water —they reduce the sulphates. Olivier[6] proved later that the sulphuraires transform sulphur directly into hydrogen sulphide. His experiments upon this are very remarkable. He takes fresh, well-washed baregin, puts it in a flask with barium chloride, and shows that hydrogen sulphide, mixed with carbon dioxide, is given off. According to him, sulphur is changed into hydrogen sulphide, under the influence of some unknown enzyme, without leaving the organism as

[1] Nastukoff : "Pouvoir réducteur des levûres pures: moyen de le mesurer. Compt. rend., **121,** 535 (1895).

[2] The fact was recently discussed before the Association de Sucrerie et de Distillerie in a communication by Emile Barbet regarding my investigations. (June 2, 1902.)

[3] L. Olivier: Bull. Soc. Bot. France, p. 29 (1882) ; A. Étard et Olivier : Compt. rend., **95,** 846 (1882) ; L. Olivier : "Sur la flore microscopique des eaux sulfureuses."

[4] See Duclaux : Traité de Microbiologie, **2,** 177. Duclaux seems to believe that philothion exists only in yeast cultures in suitable media. This is incorrect, for there are always reducing enzymes in all yeast cells, no matter how they are grown. The latter influences only the mass of the cells.

[5] The organisms are rare even in the spring itself. They are small, motile rods, very transparent and difficult to observe. The farther we go from the source, and as the water cools, it is found that the rods or filaments multiply, and at about 50° there appear the masses of baregin that are nothing but a zooglœa of rods mixed with grains of reduced sulphur upon which are developed sulphuraires similar to the filaments in the spring, but more elongated and enclosing characteristic granules of sulphur. See A. Certes et Garrigon : "De la présence constante de micro-organismes dans les eaux de Luchon, recueillis au griffon a la température de 64° et leur action sur la production de la barégine," Compt. rend., **103,** 703 (1886).

[6] L. Olivier : "Nouvelles expériences physiologiques sur le rôle du soufre chez les sulfuraires." Compt. rend., **106,** 1806 (1888).

sulphate, and the decomposition of the hydrogen sulphide by the humidity and the oxygen of the air is the cause of the precipitation of free sulphur.

Olivier has shown that there are formed by the action of glairin and of baregin, equal volumes of carbon dioxide and of hydrogen sulphide, which leads him to suppose that the sulphur bacteria assimilate at the same time sulphur and oxygen, at the expense of the alkaline sulphates, thus producing carbon oxysulphide instead of carbon dioxide. This gas then combines with water, regenerating carbon dioxide and hydrogen sulphide.[1]

All these facts lead to the conclusion that the sulphates are reduced by secretions related to philothion, and evidently acting like enzymes and hydrogenizing reducing agents. It is a matter of scientific interest to clear up this point.[2]

There exists a whole class of bacteria, the *Bacilli sulfhydrogeni* of Miquel,[3] which have the property of liberating carbon dioxide and hydrogen sulphide when grown in a medium containing either free or combined sulphur. Besides, the bacteria that can give hydrogen sulphide with free sulphur are very numerous,[4] so that this property is not to be regarded as a specific character. To show this, it is only necessary to suspend in the culture-flasks strips of paper saturated with lead acetate.[5] They frequently turn black. On adding washed flowers of sulphur to the cultures the phenomenon becomes much more marked, and streams of hydrogen sulphide are liberated.

We do not know the mechanism of this hydrogenation, but

[1] Than : Ann. Chem. (Liebig), Suppl., **5**, 236.

[2] M-Emm. Pozzi-Escot : "Mémoire sur les propriétés catalytiques des hydrogénases," Compt. rend., **134**, 81.

[3] Miquel : "Sur la fermentation sulfhydrique," Bull. soc. chim., [2], **32**, 127; "Biogenése de l'hydrogéne sulfuré par les bactéries," Ann. de Micro., 1880.

[4] Holschenikoff: "Sur la formation de l'hydrogéne sulfuré par les bactéries," Ann. de Micro., 1880.

[5] Rosenheim : Soc. de. médecine interne de Berlin, 1887. This author has found, in urine containing hydrogen sulphide, bacteria that gave off this gas when iu contact with free sulphur, and concluded, wrongly, that the odor of hydrogen sulphide detected in the urine at the moment of its emission was the result of bacterial action. We now know that the enzymes of the kidneys, which may diffuse into the uriue under certain conditions, give hydrogen sulphide when in contact with sulphur or sulphates, and that the bacteria are able to cause the same phenomenon on their own accouut.

believe it is due to the formation of nascent hydrogen. It would be interesting to see whether these organisms are not rich in reducing enzymes, as seems probable. I have not had time to verify this fact, which appears to be true, *à priori*. They have been introduced into science under the name "sulphur bacteria,"[1] since they can oxidize hydrogen sulphide and thus form deposits of sulphur.

Winogradski[2] maintains that this oxidation can proceed as far as sulphuric acid. This point is still very obscure. There is some relation, not yet evident, and a mechanism very interesting to study, between the sulphuraires and the sulphur bacteria.

Action of Reductases upon Hydrogen Peroxide.[3]

It has been known for a long time that enzymes, in general, decompose hydrogen peroxide, and it is customary to characterize the action of an enzyme by the oxidation of an emulsion of an alcoholic tincture of gum guaiacum, in the presence of hydrogen peroxide. The latter, under the influence of the enzyme, gives the oxygen necessary to transform the guaiaconic acid into guaiacum blue. I was the first to show that the action of the reducing enzymes is quite different, yet the hydrogen peroxide is decomposed, and there is a very active liberation of oxygen, amounting, with an excess of peroxide, to several hundred cubic centimeters in a few minutes. The enzyme seems, at first sight, to act like a substance having the properties of a catalytic agent.

It is interesting to note that although philothion decomposes hydrogen peroxide, it does not give the characteristic reaction with gum guaiacum in the presence of the peroxide.

---

[1] Petri and Maassen : Arb. aus dem Kaiserl. Gesundheitsamte, **8**, 318 (1893) ; Morris : Arch. für Hygiene, **30**, 304 (1897).

[2] Winogradski: Botan. Zeitung, Nrs. 31-37 (1887) ; E. Wollny : "La décomposition des matières organiques et les formes d'humus dans leurs rapports avec l'agriculture (Trad. de E. Henry)", p. 53.

[3] M-Emm. Pozzi-Escot : "Mémoire sur les propriétés catalytiques des hydrogénases," Compt. rend., **134**, 81. "Propriétés catalytiques des hydrogénases ; identification de la catalase de Loew et du philothion de de Rey-Pailhade," Bull. soc. chim. [3], **28**, 280, 288 ; "Sur un élément diastasique nouveau de l'urine," Compt. rend., **134**, 134 ; Ann. et. Rev. de Chim. analyt., **7**, 212 ; Ann. Soc. roy. méd. Gand ; "Mémoire sur les principes réducteurs des tissus vivants et leur identification avec la catalase de O. Loew."

It is well to recall that catalyzers give this reaction. Manganese dioxide gives it even in the absence of hydrogen peroxide. We may explain this anomaly by supposing that the nascent oxygen is insufficient to cause the reaction, and that there must be the intervention of another oxidizer,[1] or else that the guaiacum blue tends to be formed, but is immediately destroyed by the reducing enzyme, which would be still another proof in favor of its existence. Several facts lead us to the conclusion that the latter is the only good explanation, especially the decomposition of the previously formed guaiacum blue by the action of philothion.

In trying to discover the law of the decomposition of hydrogen peroxide, we were led to measure the amounts of oxygen set free by the same quantity of enzyme with increase of time, and to determine the influence upon this action of the substances which Duclaux calls paralyzers. The solution of enzyme that was used was prepared in the way we have already described in this article. When shaken with an excess of a twelve-volume solution of medicinal hydrogen peroxide, 10 cc. of such a solution gives, in eight minutes, 182 cc. of oxygen measured at 15° and 760 mm. We have, besides, followed the general course of the liberation throughout the experiment, with the following interesting result :

Liberation of Pure Oxygen by 10 cc., of the Solution of Hydrogenase Acting upon an Excess of Hydrogen Peroxide.

Time in seconds.	Volume in cc.	Time in seconds.	Volume in cc.
0	0	135	99
25	15	165	111
30	30	180	120
45	50	240	138
60	68	300	149
75	77	360	160
90	82	420	169
105	87	480	178
120	93	540	183.5

To make the liberation of gas more regular, the liquid was shaken almost constantly, and always before each reading. If a mechanical agitator had been used it is probable that

[1] We owe this hypothesis to Oscar Loew.

there would not have been any irregularities in the table.
The general course of the phenomenon is interesting.   At first
the action is very rapid, then it gradually becomes slower,
and finally, at the end of a variable time, the enzyme becomes
absolutely inactive.   In the following table the liberation of
gas from minute to minute is given :

Time. Minutes.	Gas set free. cc.
1	68
2	25
3	27
4	18
5	11
6	11
7	9
8	9
9	6.5

In what way does philothion cause the decomposition of
hydrogen peroxide ?   Does it act as a catalyzer, or does it at-
tack the hydrogen peroxide directly, setting free a molecule
of oxygen upon which its labile hydrogen acts, giving water
and gaseous oxygen, according to an equation analogous to
Hoppe-Seyler's ?   It is not easy to decide between these two
hypotheses.   It seems more probable that there is no catalytic
action, but rather a more or less complex chemical action, as
we must suppose from the action of the paralyzers.   It is,
without doubt, the oxidation of the hydrogenase that causes
the reaction to become slower.

It is worth mentioning that the solution of hydrogenase ob-
tained from beer yeast, by means of alcohol, has an acid re-
action.   Its acidity, calculated in terms of sulphuric acid, is
1.200 grams.

We have shown experimentally that, after acting forty
minutes upon hydrogen peroxide, its catalytic power becomes
zero.   We have also studied the influence of temperature on
the reaction.   Our experiments were carried out at 15°, and
we have shown that the action is greatest between 30° and 40°.
De Rey-Pailhade gave the latter temperature as the optimum
for philothion.   But we have found that if, at this tempera-

ture, the liberation of oxygen was more active at the beginning, there was a marked difference in the curve showing the rate of the action. At 40° the activity entirely ceases in ten minutes ; at 60° the action lasts but a few minutes ; and above 70° a large coagulum is formed, and the enzyme entirely loses its activity.

The action of paralyzers is of great interest. In the following table is shown the time necessary to obtain 40 cc. of oxygen with 10 cc. of philothion, 0.5 gram of each of the salts, and an excess of hydrogen peroxide :

Paralyzer.	Time in minutes and seconds.	
	Minutes.	Seconds.
Blank	0	45
$HgCl_2$	infinite	
$AgNO_3$	"	
LiCl	3	15
$MnCl_2$	5	3
$CaCl_2$	3	25
NaCl	5	8
KCl	5	12
H_2KPO_4	4	54
KNO_3	11	20

In a general way, the most energetic paralyzers are the salts with an acid reaction; then come the nitrates. Mercuric chloride and silver nitrate have a very powerful depressive action. A solution giving, in a blank experiment, 180 cc. of oxygen in nine minutes gave, in the case of mercuric chloride, only 5 cc. of oxygen in four minutes, at the end of which time the action had apparently ceased. With silver nitrate 3 cc. were obtained in five minutes. In large excess, chloroform has a noticeable paralyzing action. The following shows the course of the experiment :

Time in seconds.	Oxygen set free.
	cc.
30	18
60	23
120	26
180	33
240	39
300	45

A blank experiment gave 180 cc. of oxygen in nine minutes.

An experiment was carried out with a large excess of chloroform (see table on page 546).

The following results were obtained with ferrocyanide :

Time in seconds.	Oxygen set free. cc.
30	25
60	35
90	50
120	60
150	70
180	75
210	78
240	81

The following figures were obtained with calcium chloride.

Time in seconds.	Oxygen set free. cc.
15	12
30	17
45	18.5
60	20
120	22
180	39
240	51
300	58
360	62

As I have already stated, the solution of the enzyme which was used in these experiments had an acid reaction. However, the addition of any considerable amount of a mineral acid or a strong organic acid, such as acetic acid, acts as a strong paralyzer. On the contrary, traces of alkali are very active, provided the alkalinity is very slight. The following experiment shows this :

A blank gave, in one minute, 25 cc. of oxygen.

With 0.5 cc. of acetic acid there were set free 12 cc. of oxygen.

With 0.5 cc. of ammonium carbonate there were set free 38 cc. of oxygen.

In the preceding experiments it would have been better to have worked with neutral solutions, but the results are com-

parable, nevertheless, for all the solutions had the same initial acidity.

The power of decomposing hydrogen peroxide to the extent seen in the case of philothion is not possessed by any other enzyme, to my knowledge, except by one of a new order, just made known by Oscar Loew, that I have studied. The commercial enzyme, taka-diastase, which is a commercial article extracted from *Aspergillus Orizæ*, has the same catalytic action towards hydrogen peroxide. But it is a mixture of enzymes that have not yet been well characterized and in which I have recently discovered the reductase, jacquemase.

The enzyme discovered by Loew, and named catalase by him,[1] is characterized by its catalytic action towards hydrogen peroxide. It is found in vegetable organs. Struck by the close resemblance of philothion and catalase in their action on hydrogen peroxide, alone and in the presence of paralyzers, I thought it well to study this enzyme and compare it with philothion.

A solution of catalase was prepared according to the directions of Loew,[2] as follows : We obtained several leaves of tobacco, dried in the open air, and some tobacco stems, also dried at the ordinary temperature, from a Belgian plantation. After being finely chopped, 500 grams were digested in 200 cc. of water containing chloroform. The extract thus obtained gave a precipitate of the enzyme when saturated with ammonium sulphate. A second solution was prepared from magnolia leaves. In this case the enzyme was not precipitated but the solution was used at once.

The catalytic enzyme thus obtained corresponded to the form β of Loew. There is no real difference between the form α and the form β of Loew, and the distinction established by him has no scientific value.[3] An experiment was made in order to determine the catalyzing power of the en-

---

[1] M-Emm. Pozzi-Escot : "Sur une nouvelle diastase," Rev. gén. de chim., **5**, 182, 194.

[2] Oscar Loew : U. S. Dept. Agr. Rep., No. 68, p. 39 (1901).

[3] Loew made a hypothetical distinction without great value, in my opinion. The soluble form of catalase was called β, and the insoluble form α; that is, one form can be extracted with water and the other cannot. He seems not to understand the property of adherence which is peculiar to the enzymes.

zyme thus obtained. To 10 cc. of the active solution was added an excess of hydrogen peroxide, and the oxygen set free was measured as in the experiments with philothion. There were obtained the following results :

Time. Minutes.	Oxygen. cc.
1	15
2	22
3	26
4	28.4
5	30
10	33.4
15	35
20	36.7
25	38

The figures are lower than those obtained with the extract of beer yeast, but they are of the same order as those cited by Loew.

An experiment carried out to see whether the enzyme obtained by Loew, and which we prepared for our work, was able to hydrogenize sulphur, gave a positive result. So far there is no difference between the general properties of Loew's catalase and philothion. One point, however, remained to be cleared up. Loew described catalase as an oxidase. Would it be possible to obtain oxidation by means of philothion ? *A priori*, it did not seem impossible, for every reduction is the correlative of an oxidation. Besides, we often find catalytic properties and oxidizing power combined, well-known instances being platinum black and manganese peroxide. Platinum black can also cause reduction, for it reduces ammonium nitrate in the presence of glucose which is, at the same time, oxidized. Hence, the idea of an enzyme having both reducing and oxidizing power is not a new one. Philothion and catalase are without action on an alcoholic tincture of gum guaiacum, but that is not sufficient evidence. We have also tried all the known reactions of enzymes, but without result. The reaction with tetramethylparaphenylenediamine failed, and the reactions with indophenols and tyrosine indicated nothing. This does not mean that a reducing en-

zyme cannot yield oxidation-products. These have been noticed, but they are the result of a secondary reaction. Our results only show that, towards these reagents, philothion and catalase do not act in the same way.

Loew claims to have oxidized hydroquinone,[1] which I did not succeed in doing, no matter what means were employed. The hydroquinone was oxidized neither by Loew's enzyme nor by a very active solution of philothion.

It should be stated that Loew found that catalase, when of animal origin, caused perceptible oxidation, but none at all when it was obtained from plants. An oxidizing agent might also have been concerned in the experiments of Loew. However, from his results, it seems to me that catalase is a reductase and is identical with philothion. If we consider the results obtained in the decomposition of hydrogen peroxide by philothion and by catalase, one is struck by their close agreement, which would not be the case with two different enzymes. It has also been shown that the optimum temperature is practically the same for each of them, which is a criterion of the first order. Both give hydrogen sulphide with free sulphur, both have strikingly similar reducing action, and both are found in the same organs. It seems, then, justifiable to conclude that Loew's catalase is identical with the enzymes of the new group which I have established. In my article on the subject[2] is given all that is known of catalase.

Catalytic Properties of Fibrin.[3]

The catalytic properties of fibrin, observed by me, led me to investigate whether the decomposition of hydrogen peroxide by fresh fibrin was not a reaction of the same order. We know with what ease the enzyme complexes attach themselves to certain substances.

Fibrin was first made from large quantities of blood, taking all the precautions recommended in the memoirs on the subject. It was shown that the very active fibrin thus obtained

[1] Oscar Loew : U. S. Dept. Agr. Rep., No. 68, p. 39 (1901).

[2] M-Emm. Pozzi-Escot : "Sur une nouvelle diastase," Rev. gén. de chim., **5**, 182, 194.

[3] M-Emm. Pozzi-Escot : " Sur les hydrogénases du sang et les propriétés catalytiques de la fibrine," Compt. rend., **134**, 446 ; Bull. de l'Acad. de Médecine, March 25, 1902 ; Bull. soc. chim. [3], **27**, 449 ; Ann. soc. Méd. de Gand, July, 1902.

yields to suitable solvents a substance with catalytic and re-
ducing properties. Hence fibrin is the vehicle, in the blood,
of the reducing enzymes that it protects, and the activity of
which it moderates more or less completely. When extracted
from the blood, the fibrin carries with it the greater part of
the reductases.[1]

Action of Physical Agents.

Heat accelerates the action of the reductases, up to 45°.
This seems to be the optimum for philothion, as well as for
jacquemase. At about 60° the activity of the enzyme seems
suspended. Loew maintains, nevertheless, that the enzyme
that I have identified with the reductases resisted the action
of boiling absolute alcohol (78°) for twenty seconds. I have
not had an opportunity to verify this fact.

My experiments on the action of light are not yet com-
pleted. It seems to me that the reductases obey the general
law, and decompose much more rapidly in direct sunlight than
in a diffused light or in darkness.

I have tried to study the action of electricity,[2] but it is very
difficult to distinguish the effect of the electricity from the
heat produced by the passage of the current, according to the
law of Joule, and also to avoid the action of the salts used to
carry the current. In the vessel used for the electrolysis we
may isolate the electrodes, and consider the intermediate part,
alone, as acted on by the current, but we know that the ions
move throughout the entire liquid, and there is nothing to
show that they do not act under these conditions. A long-
continued current, if relatively intense and passed long
enough, destroys the action of the enzyme.

The Reductases as Oxidizing Agents.

The internal mechanism of the possible action of the redu-
cing enzymes is a subject of interest. My own investigations
on the subject are hardly begun, and I can only mention a
few facts here and there for lack of time.

[1] M-Emm. Pozzi-Escot: "Sur les principes réducteurs des tissus vivantes, et les
propriétés catalytiques de la fibrine," Bull. général de thérapeutique, **142**, 764.

[2] M-Emm. Pozzi-Escot: "Action du courant électrique sur les hydrogénases,"
Compt. rend., **134**, 678.

The following quotation from the note by which Armand Gautier introduced two of my papers before the Academy of Medicine, will serve to introduce this paragraph.[1] His explanation will make clear the great importance of the problem : " A young and very active scientist of Nancy, M-Emm. Pozzi-Escot, asks me to present to the Academy two interesting memoirs entitled, ' Catalytic Properties of Hydrogenases,' and ' Contribution to the Study of the Reducing Substances in Living Tissues.' The author recalls that in 1888 de Rey-Pailhade discovered in living tissues, in yeast and, in general, in young cells, a substance which could cause reduction, that he called philothion on account of the property it possessed of liberating hydrogen sulphide in the presence of free sulphur. He found later that this substance acts like a hydrogenizing ferment. It was, in fact, a hydrogenase.

" Starting from these remarkable observations, Pozzi-Escot studied the part played by this hydrogenizing ferment, and concluded, especially from his work on beer yeast, in which the ferment is quite abundant, that it has the double property, on the one hand, of reducing directly or of hydrogenizing organic substances in the tissues, and on the other, of oxidizing them by a reaction indirectly foreseen by Hoppe-Seyler, which consisted in decomposing a molecule of free oxygen or that which is so lightly held by an inactive molecule of haemoglobin that it is still composed of 2 atoms. But in the presence of the hydrogenase, one of these atoms unites with hydrogen from the ferment to form water, while the other is set free in the nascent state or as an ion, and has active oxidizing power.

" Pozzi-Escot identified his hydrogenase with philothion, and with catalase, obtained by Loew from tobacco leaves and which he believed to be an oxidizing ferment, and showed that it acted like a true hydrogenase. Finally, he showed that the hydrogenase exists in the blood, and that it combines with the fibrin as it coagulates.

" The existence of hydrogenases in living tissues has been confirmed, besides, by Gérard and Abelous for the kidney, a

[1] Armand Gautier : Bull. Acad. Médecine, Paris, [3], **47**, 400 (1902).

fact that makes of still greater importance the views I expressed long ago concerning the internal mechanism of the reactions taking place in the protoplasm of the living cell. The reactions that take place in its depths, far from being phenomena of oxidation, as has been thought since the time of Lavoisier, are phenomena of hydrolysis and of reduction. The oxidations do not take place until later, and only in the external or superficial parts of the cell, and at the expense, not of the protoplasm itself, but of its decomposition-products formed by the first stage of the vital function."

We know, in a general way, that certain oxidizing or reducing processes are reversible under certain conditions. We need only mention the oxidizing power of platinum-black and its reducing action towards nitrates, which it transforms into ammonia under certain conditions.[1]

The process of oxidation in the blood has been studied by many authors, all of whom have had in mind the action of an oxidase. It has been found that a pulp made from the organs of different animals, or even the extract prepared from them, can oxidize benzoic aldehyde, salicylic aldehyde, and formic aldehyde, transforming them into the corresponding acids. Methyl alcohol can be oxidized, but less readily, into formic acid, benzyl alcohol into benzoic acid, and even the oxidation of acetone and uric acid has been observed.

Spitzer also attributes to the action of oxidases certain color reactions, such as the formation of indophenols, of Bindschedler's green, and of toluene-blue. Binz showed that animal extracts can transform arsenious acid into arsenic acid. These so-called "oxidasic" oxidations are generally of a singular nature. Pohl prepared two extracts that would oxidize aldehydes but not give the indophenol reaction. Jacobs decomposed uric acid by means of dog's liver, but not with that of a calf. Spitzer also found that glucose is oxidized by the blood and by various extracts of animal tissues. The enzyme that caused these oxidations was called the glycolytic ferment and Spitzer said that it gave a blue color with an alcoholic tincture of gum guaiacum, and had, at the same time, a catalytic action on hydrogen peroxide.

[1] Ber. d. chem. Ges., **23**, 675 (1890).

Jacobs, although he cast a doubt upon this view, admits the existence of several oxidizing enzymes in animal tissues, and believes, also, that the enzyme that causes the oxidation of sugar is different from that which transforms benzoic aldehyde into benzoic acid.[1]

It must be remembered that, in many cases, the action of the enzymes is specific; that is to say, they act on certain classes of substances containing groupings, the reactivity and even the configuration of which corresponds to that of the enzyme.[2]

If, as we believe, the reductases are susceptible of producing oxidations and reductions at the same time, this would take place only with substances upon which the enzyme could not act as a reducing agent without rapidly reaching a state of equilibrium, a limit closely dependent upon the conditions of the reaction.

This is what takes place usually. If we wish to show clearly the secondary oxidations (see the definition of Armand Gautier), it is absolutely necessary to employ certain experimental methods that remove as far as possible the limit of the reaction.

We have seen that oxidations by means of oxidases are possible only at the exterior of the cell or of the tissues and that, whenever internal oxidation takes place, it is due to a secondary action closely dependent, in some way difficult to conceive, upon a reducing enzyme.

I was led to the observation of these remarkable phenomena by an investigation carried out to see whether oxidizing enzymes exist in the cells of beer yeast. It has been stated that oxidases exist in this organism, but no real proof of it could be cited. It was only because, from its superficial properties, it acts like an agent of combustion. Duclaux stated that some oxidase exists in Buchner's press-juice.

The subject is still very perplexing, for the yeast acts like a plant. It respires, and the respiratory quotient, $\dfrac{CO_2}{O}$, may have, according to the vital condition, a value varying from

---

[1] Jacobs : Virchow Archiv., **157**, 235 (1899).
[2] This last condition is given with all due reservation.

unity to infinity. At first sight the yeast cell seems to be aerobic, on account of the secretion of oxidases. This was the leading idea in the investigations of Effront and Grüss, which are, however, inexact. I sought these oxidases at first in the extract of yeast, but this is such a reducing agent that one is bound to fail in trying to detect any oxidizing action. One must not be deceived and admit certain experiments as exact, for the reductases have very great vitality, much greater than the oxidases. This is, I think, an objection to certain of the experiments of Grüss, which I criticized when they were published,[1] and to which I will not return.

I have also tried to detect the presence of oxidizing secretions by working with actively growing yeast, but with complete lack of success, for in this condition, also, the yeast causes reduction, and takes up oxygen readily. On the one hand, the cell-sap of the yeast is essentially a reducing agent, and under no circumstances can it produce oxidation.[2] On the other hand, the living cell causes reduction, and absorbs the oxygen, which it needs to continue its growth, from the oxygen compounds around it.

Grüss and Effront had, nevertheless, characterized certain oxidizing secretions of the yeast cell. I think I have shown this to be wrong, but it led me to see whether the reductases might not, under certain conditions, act as indirect oxidizing agents. With this end in view, I made the following experiments :

1. Five hundred cc. of a very active solution of de Rey-Pailhade's hydrogenase, prepared as already described, were put into a 750 cc. flask, then 1 gram of salicylic aldehyde was added. The flask, incompletely filled, was closed and so shaken as to bring all of the liquid in contact with the oxygen it contained. At the end of several hours the liquid was made alkaline with sodium carbonate and evaporated to dryness in an air-bath at 105°. The residue was washed with 200 cc. of 90 per cent alcohol, in several portions, and the solution obtained evaporated to a small volume. The residue

---

[1] "Sur les oxydases de la levûre," Compt. rend., **134,** 377 : Revue Oenophile, **9,** 118.

[2] It all depends on the manner of life of the cells studied. From this point of view there are very great differences between them.

was acidified with hydrochloric acid and extracted with ether. The ethereal solution, when poured off and evaporated, yielded a small amount of salicylic acid. It is a question whether this oxidation is the result of a primary or secondary reduction by the reductase.

2. Experiments were made in all respects similar to the one above, but to the solution was added some easily reducible substance, such as an iodate, an arsenate, etc. Under these conditions, and working in the same way, the amount of salicylic acid formed was increased. From this we must conclude that the oxidation was due to a secondary action accompanying the true reduction.

3. Several other series of experiments were made in which benzyl alcohol was the substance oxidized. The results were conclusive, for in no case was any benzoic acid formed.

These experiments are not satisfactory, but they are interesting, and for that reason have been mentioned.[1]

Physiological Rôle of the Reductases.

Reducing agents are as important in the organism as oxidizing agents, and the importance of the reductases is also considerable.[2] The phenomenon of disassimilation is intimately connected with these secretions. De Rey-Pailhade wished to treat the subject in the preface to my work, but I only mentioned the occurrence of these enzymes in the urine.[3] They come from the kidneys, and can pass into the urine only as the result of a physiological accident. This has been brought to the attention of physiologists.

From another point of view the reductases play an important part in nature. I have shown that they decompose hydrogen peroxide, giving free oxygen. Also the investigations of de Rey-Pailhade and myself have shown that they are very abundant in plants and animals. There must be some reason

[1] I showed recently that yeast contains spermine, thus demonstrating an inaccuracy in the theory of Grüss.

[2] De Rey-Pailhade : Bull. général de Thérapeutique, **142**, 17. See also "Rôle du philothion dans le mécanisme de l'action des médicaments," *Ibid.*

[3] J. A. Vandevelde : "La catalase," Bull. Soc. Médecine de Gand (1901) ; Over de vers preidino von catalase. Pozzi-Escot : "Sur un element diastasique nouveau de l'urine," Compt. rend., **134**, 1332 ; Ann. et. Rev. Chim. analyt., **7**, 212 ; Ann. Soc. Médecine de Gand, June 5, 1902.

for this abundance. May it not be due, in part, to their action on hydrogen peroxide ? It is known that this is a powerful antiseptic, the presence of which in the cells would be sure to kill them.[1] According to my supposition, the reductases in the cells destroy all traces of this substance as soon as it is formed, and before its presence becomes harmful.

It cannot be denied that hydrogen peroxide is probably formed in the cell during respiration. Recent experiments have proved that labile hydrogen atoms in an organic compound are able to form hydrogen peroxide when in contact with free oxygen.[2] If it is really produced under these conditions, the reductases must prevent its accumulation by destroying it, and the oxygen set free will be used in the process of respiration.

The protoplasm of the cell is of a very complex organization composed of easily modified proteids. The easy transformations into relatively stable substances during the processes of assimilation and disassimilation are due to the loss of labile atomic groupings by molecular migration, and to a loss of kinetic energy. This energy is transmitted by the protoplasm to thermogenic substances, principally sugars and fatty substances (lecithine), which cannot be directly oxidized at the ordinary temperature. But in contact with the protoplasm these substances can be directly oxidized, for the protoplasm imparts to their constituent atoms so much energy that their reciprocal affinities are augmented, and they become able to combine directly with oxygen, without the necessity of its being first changed into a more active form. The breaking-down of the oxygen molecule, and the union of its atoms with the labile atoms of the sugars and fatty substances, take place at this moment. But, at the same time, certain atoms of hydrogen and thermogenic substances that have become labile

---

[1] See Beaudet : "De l'eau oxygénée et de ses emplois," Bull. Chim. de Sucrerie et de Distillerie, 1898-1899, p. 924. Macé : Traité de Bactériologie, 4ᵉ Edit. Des agents chimiques, p. 66. Bert et Regnard : "Influence de l'eau oxygénée sur la fermentation," Compt. rend., **94**, 1383 (1882).

[2] See Bamberger : Ber. d. chem. Ges., **33**, 113 ; W. Manchot : " Ueber freiwillige Oxydation," Leipzig, 1900. Engler : Ber. d. chem. Ges., **33**, 1103. Baeyer : *Ibid.*, **33**, 1582. O. Loew : "Die chemische Energie der lebenden Zellen," München, 1899. Reinke : Botan, Zeitung, **41**, 66. 90 (1883).

and charged with energy, may combine with the remaining molecules of oxygen, thus forming hydrogen peroxide as a secondary product. The heat produced by the combustion of the thermogenic substances is transformed to a certain extent into chemical energy by the living protoplasm. This energy facilitates the changes of valence of the atoms, for it increases the amplitude of their vibrations.

By analogous theoretical considerations, it would be possible to show that the respiration of the tissues can be regarded as partly due to the preliminary formation of hydrogen peroxide.

An ingenious theory of Erlenmeyer will serve to explain my idea of the assimilation of carbon in plants. Is the formation of carbohydrates in plants closely connected with the presence of enzymes like the reductases? Such a thing would not be surprising,[1] and if we will recall the facts that have been given, it will be easily seen by what an unbroken series of logical deductions we are led to consider this hypothesis as plausible, *à priori*, and even as well established. The carbohydrates are synthetic products resulting from the general nutrition of the green cells of plants, or just the cells in which the enzymes are produced.

It is generally admitted that the oxygen is set free by the plant by a reaction somewhat like the one below, where we see the carbon dioxide combining with a molecule of water, and forming first formic aldehyde and then oxygen.[2]

$$CO_2 + H_2O \longrightarrow O = C \Big\langle {}^{OH}_{OH} \quad \longrightarrow \quad O = C \Big\langle {}^{H}_{H} + O_2.$$
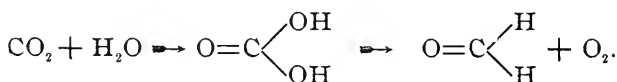
Erlenmeyer tried to explain the separation of oxygen by the intermediate formation of hydrogen peroxide,[3] and regarded formic acid as the first product in the assimilation.

---

[1] It may be that the enzymes that cause the formation of the sugars, and which Emile Barbet has called (hypothetically) "saccharogenic," are quite different. This seems to be very probable. See E. Barbet: "Sur l'hypothèse d'une diastase saccharogénique," Bull. chim. de Sucrerie et de Distillerie, p. 634, 1898–1899; pp. 582, 839, 1897–1898.

[2] P. Mazé: "L'assimilation du carbone et de l'azote dans le monde vivante," p. 33.

[3] Erlenmeyer: Ber. d. chem. Ges., 10, 634 (1877).

$$O=C{<}^{OH}_{OH} + {}^{OH}_{H}\ \ \dashrightarrow\ \ O=C{<}^{H}_{OH} + HO-OH$$

$$\begin{array}{l} HO-OH \\ \qquad\qquad \dashrightarrow\ \ 2H_2O + O_2. \\ HO-OH \end{array}$$
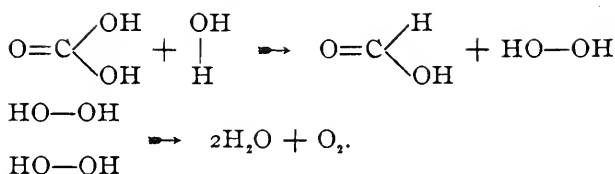
However, the formation of formic acid is not at all certain, and does not appear very probable,[1] so that, for the preceding equations, we may substitute the following :[2]

$$O=C{<}^{OH}_{OH} + {}^{HOH}_{HOH}\ \ \dashrightarrow\ \ O=C{<}^{H}_{H} + {}^{H_2O_2}_{H_2O_2};$$

$$2H_2O_2 = 2H_2O + O_2.$$
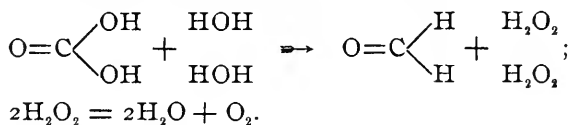
In conclusion, all that precedes is hypothetical, but the catalytic properties of the reductases, their abundance in all growing organs, the more than probable formation of hydrogen peroxide, and its harmful action, may support my explanations.

All the theories have, in common, the formation of formic aldehyde which polymerizes to form saccharose. The volume of oxygen set free corresponds to the volume of carbon dioxide, the carbon of which entered the formic aldehyde. The theories have not been verified experimentally, although the work of Fischer on the synthesis of the sugars gives them a solid basis of fact. I have shown in what way the catalytic power of the reductases might exert itself. Is this catalyzing force the only one that intervenes, and do the reductases not reduce in the presence of other substances? *À priori*, this seems plausible. It must be admitted that formic aldehyde is not always found in the leaves. Does it polymerize at once, as seems probable from its toxic properties? Or might it not at once form an albuminoid compound, with the properties of an aldehyde, which would be the reductase in question, and would not be toxic? This formation of aldehydes is to be compared with the reduction of the nitrates or of the ammonium salts, whence, by mutual reaction, the nitrogen enters the organism, and quaternary compounds are formed.

[1] Pfeffer: "Physiology of Plants," **1**, 356 (1900).

[2] M-Emm. Pozzi-Escot: "Sur une nouvelle diastase," Rev. générale de chim., **6**, 182, 194.

Abundance of the Reductases in Nature.

The reducing enzymes are very abundantly distributed in the animal and vegetable kingdoms. De Rey-Pailhade showed how frequently philothion occurs in animal tissues,[1] by estimating the amounts of hydrogen sulphide set free by them when in contact with an excess of sulphur. Nearly all the organs contain philothion. The white of egg deserves especial mention. When ground with sulphur it at once yields a great deal of hydrogen sulphide. If the white be treated with alcohol it coagulates, and no longer produces hydrogen sulphide when in contact with sulphur.

The yolk, on the contrary, yields no hydrogen sulphide with sulphur alone, and its amount is increased at the first instant by the addition of alcohol.

The reductases exist in the blood, where they attach themselves to the fibrin, to which they impart catalytic properties.

I have also shown that the reductases and Loew's catalase are identical. Loew found his enzyme in a number of plants, some of which had been dried for a long time. A very complete résumé of these experiments was published by the Department of Agriculture in Washington, in 1901. A review of it was published by me.[2] I verified personally the statements of Loew, and showed that reductases are to be found in all growing tissues.

Fruits contain reductases. The pulp of acid fruits is generally poor in reductases, but the seeds may be very rich in them. It has also been found that in oily seeds the proportion of enzyme is greater than in the others. During germination the proportion of enzyme is greatly increased. In the molds large quantities of reducing enzymes are often met with. These enzymes are relatively very vigorous, and they keep well in solution in glycerol, or in weak alcohol, in the presence of antiseptics. In time they are destroyed by the absorption of oxygen.

Jacquemase, which I discovered in koji (Japanese yeast),[3]

[1] De Rey-Pailhade : ''Recherches experimentales sur le philothion,'' (1891).

[2] M-Emm. Pozzi Escot : ''Sur une nouvelle diastase, la catalase ; son rôle dans la nature,'' Rev. gén. de chim., **5**, 182, 194.

[3] M-Emm. Pozzi-Escot : ''Sur une nouvelle diastase réductrice, extraite du Koji Japonais et secretée par l'*Eurotium Orizæ*,'' Compt. rend., **134**, 753 ; Bull. soc. chim., **27**, 557.

is secreted by *Eurotium Orizæ*. It is easily distinguished from philothion, because it does not give hydrogen sulphide when in contact with sulphur. I have called it jacquemase in honor of G. Jacquemin, in whose laboratory I discovered it. It has all the properties of the other reductases except the power to form hydrogen sulphide in the presence of free sulphur. It changes nitrobenzene into aniline to a considerable extent. It is very abundant in nature, and especially exists in many tubers.

Béhal, of Paris, suggested calling it "*eurotase*" to recall its origin, in conformity with the principles of classification proposed by Em. Bourquelot. It did not seem necessary to do this, for jacquemase, which was discovered in *Aspergillus Orizæ*, is not confined to that mold, but is also found in a large number of others, and exists in abundance in many of the higher plants. Besides, the name "eurotine"[1] has already been suggested for the liquefying enzyme of *Aspergillus Orizæ*. Eurotine thus becomes a eurotase (Duclaux). In order to avoid this regrettable confusion, it seems to me more practicable to retain the first name.

Laboratoires de Recherches de
Chimie Pure de G. Jacquemin,
Malzéville, France.

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE.

PART II.

(Continued from the May Number.)

By J. H. Kastle and A. S. Loevenhart.

AS TO THE MODE OF ACTION OF HYDROGEN PEROXIDE AS AN OXIDIZING AGENT, AND ITS CATALYTIC DECOMPOSITION BY VARIOUS SUBSTANCES.

Any satisfactory inquiry into the manner in which hydrogen peroxide acts as an oxidizing agent must take into account the following facts:

1. Hydrogen peroxide is capable of oxidizing certain substances directly and without the intervention of an oxygen

[1] Neuville: "Les ferments industriels d'Extrême Orient," p. 113.

carrier,[1] and without the evolution of oxygen gas. Among the substances which it can thus oxidize may be mentioned the following : Sulphurous acid, ammonium sulphocyanate,[2] phenolphthalin, and formic aldehyde. We have elsewhere pointed out that, whereas, at low temperatures formic aldehyde is oxidized by hydrogen peroxide with evolution of small amounts of oxygen, at high temperatures this oxidation proceeds very rapidly and without the formation of molecular oxygen.[3]

2. In certain oxidations by hydrogen peroxide, especially in the presence of oxygen carriers, oxygen gas is evolved simultaneously with the oxidation, and in certain instances, notably in the oxidation of the nitrils, as has been pointed out by Radziszewski,[4] the same quantity of oxygen leaves the system as molecular oxygen as that which remains in it in combination in the products of the oxidation. For example, according to this observer, the oxidation of a nitril by hydrogen peroxide in alkaline solution takes place in the following manner :

$$RCN + 2H_2O_2 = RCONH_2 + H_2O + O_2.$$

3. A large number of oxidations, which cannot be effected by hydrogen peroxide alone, can be readily brought about by this oxidizing agent in the presence of oxygen carriers. Numerous instances of this sort of change might be given. A good example is furnished in the case of the oxidation of formic acid studied by us, the results of which are given in Part I. of this paper, p. 434.

[1] By an oxygen carrier is here meant a substance which will enable hydrogen peroxide to effect certain oxidations which cannot be accomplished at all, or at least only slowly, by the hydrogen peroxide alone. Such a substance is ferrous sulphate.

[2] We have observed that ammonium sulphocyanate is very readily oxidized by hydrogen peroxide at ordinary temperatures, with the production of acid ammonium sulphate and hydrocyanic acid.

It has been observed also that the mixtures of ammonium sulphocyanate and hydrogen peroxide give a blue color with guaiacum, thereby indicating that ammonium sulphocyanate can act as an oxygen carrier in the presence of hydrogen peroxide. It has been found also that a solution of ammonium sulphocyanate undergoes a gradual oxidation on exposure to the air, giving rise to a small amount of a reddish substance, which imparts a pink color to the solution. It is well known that solutions of ammonium sulphocyanate gradually acquire a pink color. Such solutions have been found to turn guaiacum blue directly.

[3] J. Am. Chem. Soc., **21**, 262 (1899).

[4] Ber. d. chem. Ges., **18**, 355 (1885).

Fenton[1] and his co-workers have also investigated a large number of these cases. They have shown that a large number of polyacid alcohols and polybasic organic acids, such as tartaric, glycolic, lactic, glyceric, etc., while not acted on by hydrogen peroxide alone, are readily oxidized by it in the presence of ferrous iron. Emil Fischer has also employed ferric acetate in effecting the oxidation of certain compounds in the sugar group by means of hydrogen peroxide.

Brode[2] has also pointed out that ferrous sulphate and molybdic and tungstic acids enormously increase the rate of oxidation of hydriodic acid by hydrogen peroxide.

4. Hydrogen peroxide apparently acts as a reducing agent under certain conditions. Under this head may be mentioned its action on silver oxide, as the result of which metallic silver is formed. Instances of this are also furnished by the formation of manganous and plumbous chlorides as the result of the action of hydrogen peroxide on manganese peroxide and lead peroxide in hydrochloric acid solution, and by its action on potassium permanganate in acid solution.

5. It has been pointed out above that those substances which have the power of inducing oxidations by means of hydrogen peroxide are also capable of effecting its catalytic decomposition under certain conditions. In fact, oxidation by hydrogen peroxide in the presence of a catalyzer and its catalytic decomposition often go hand in hand, so that the latter process, as has been pointed out by Spitzer, is often a measure of the former. In our opinion all of these phenomena, widely differing as they appear at first sight, are in reality closely correlated, and referable to a common cause, namely, the tendency on the part of hydrogen peroxide to unite directly with oxidizable substances, thereby forming either a peroxide or some other complex, unstable holoxide derivative, which tends to part with its oxygen more easily than the hydrogen peroxide itself. This derivative, therefore, readily oxidizes some other substance, to which it stands in the relation of an oxygen carrier, or gives

---

[1] Fenton and Jackson : J. Chem. Soc. (London), **75**, 1 (1899) ; Fenton and Jones : *Ibid.*, **77**, 69 (1900).

[2] Ztschr. phys. Chem., **37**, 257 (1901).

up molecular oxygen, or both. It is important for this assumption, of course, that such higher oxides and unstable addition-products of hydrogen peroxide with other substances should actually exist. In reality, we have abundant proof of their existence. In fact, as may be seen from the following, many such compounds are known. In 1878 Schöne[1] isolated a number of compounds of hydrogen peroxide and the alkalies and alkaline earths, such as the following :

$$BaO_2.H_2O_2 \quad \text{or} \quad H_2BaO_4 ;$$
$$K_2O_2.2H_2O_2 \quad \text{or} \quad H_4K_2O_6 ;$$
$$Na_2O_2.2H_2O_2 \quad \text{or} \quad H_4Na_2O_6.$$
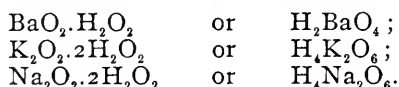
All of these compounds were found by this observer to be very unstable, and are obtainable in a state of purity only at very low temperatures. He therefore explained the catalytic decomposition of hydrogen peroxide by alkalies by the assumption that these hydrogen peroxide addition-products with the alkalies are first produced, thus :

$$2ROH + 3H_2O_2 = H_4R_2O_6 + 2H_2O ;$$
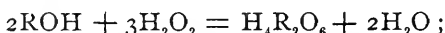
and that these substances then undergo the following transformations :

$$(1) \quad R_2H_4O_6 = R_2O_4 + 2H_2O ;$$
$$(2) \quad R_2O_4 + H_2O = 2ROH + O_3.$$
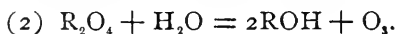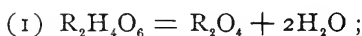
He was led to assume the intermediate production of such peroxides as R_2O_4, for the reason that the compounds such as $H_4K_2O_6$ turned yellow during their decomposition.

The work of Schöne on these complex addition-products of hydrogen peroxide has been confirmed by the later researches of Forcrand,[2] who has obtained evidence not only of the existence of such compounds as H_2BaO_4 and H_2CaO_4, but also of still more complex derivatives, such as $CaO_2.10H_2O_2$.[3]

[1] Ann. Chem. (Liebig), **192**, 257; **193**, 241 (1878).

[2] Compt. rend., **130**, 716 (1900).

[3] Forcrand represented the compound $CaO_2.H_2O_2$ by the formula $Ca(O—OH)_2$, thereby indicating that it sustains the same relation to hydrogen peroxide, $H—O—O—H$, that calcium hydroxide, $Ca(OH)_2$, does to water, $H—O—H$. This is in harmony with the idea first advanced by Traube, that in slow oxidation the molecule of oxygen (O_2) can function as the atom, and that in the true peroxides we have a class of compounds in which the molecule of oxygen (O_2) takes the part of the atom in the oxides. For these compounds Traube proposed the name "holoxides."

Similarly, Berthelot[1] observed that on adding hydrogen peroxide to potassium dichromate in the presence of dilute ammonia, a yellow precipitate was obtained containing hydrogen peroxide in combination with chromic oxide and chromic anhydride, and Moissan,[2] from his investigation of

It would seem that the value of this classification and the importance of this idea have not been generally recognized. As a matter of fact, however, it not only affords a very satisfactory means of classifying the peroxides, but it also points to the existence of a large number of derivatives of hydrogen peroxide, which sustain to this substance essentially the same relation that the oxides and hydroxides sustain to water. The following compounds are examples of this kind of combination. For the sake of clearness they are compared with the oxides and hydroxides in the following scheme of classification :

Atomic oxygen, O.		Molecular oxygen, O_2.	
Water, H_2O.		Hydrogen peroxide, $H_2(O_2)$.	
Oxides.	Hydroxides.	Holoxides.	Hydroholoxides.
M.O	M.OH	$M_2(O_2)$	$M.((O_2)H)$
K_2O	K.OH	$K_2(O_2)$	$KH((O_2)H)_3$
Na_2O	NaOH	$Na_2(O_2)$	$Ca((O_2)H)_2$
CaO	$Ca(OH)_2$	$Ca(O_2)$	$Na_2H((O_2)H)_3$
PbO	$Pb(OH)_2$	$Pb(O_2)$	
Ag_2O	AgOH	$Ag_2(O_2)$	
BaO	$Ba(OH)_2$	$Ba(O_2)$	

According to this view of the nature of the peroxides, perchromic, persulphuric, and percarbonic acids and their salts are to be regarded as mixed compounds belonging both to the hydroxides and the hydroholoxides and referable to the type

$$R{\Large\langle}_{(O_2)H}^{OH}.$$

Thus we have :

$$\text{Perchromic acid, } H_2CrO_5, \quad \text{or} \quad CrO_2{\Large\langle}_{(O_2)H}^{OH};$$

$$\text{Persulphuric acid, } H_2S_2O_8, \quad \text{or} \quad S_2O_5{\Large\langle}_{(O_2)H}^{OH};$$

$$\text{Percarbonic acid, } H_2C_2O_6, \quad \text{or} \quad C_2O_4{\Large\langle}_{(O_2)H}^{OH}.$$
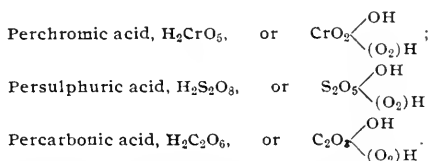
It will be observed that the formulas proposed for perchromic and persulphuric acids correspond exactly with those in general use for chromic and pyrosulphuric acids,

$$CrO_2{\Large\langle}_{OH}^{OH} \qquad \text{and} \qquad S_2O_5{\Large\langle}_{OH}^{OH},$$
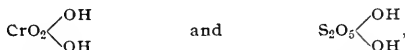
the only difference being that these peracids contain in the place of one of the hydroxyl groups a hydroholoxide group, $(O_2)H$, which latter allies them to hydrogen peroxide and affords an explanation of their powerful oxidizing properties. From these considerations one would naturally be led to expect the existence of a corresponding holoxide and hydroholoxide for every oxide and hydroxide now known. When we consider the great instability of these compounds, however, it is scarcely to be wondered at that comparatively so few of these compounds are known. That they are formed in the processes of autoxidation and in reactions with hydrogen peroxide can scarcely be denied, and we have only to admit their formation in order to explain practically all the complex phenomena of autoxidation, oxidation by hydrogen peroxide, and the effect of oxygen accelerators thereon.

[1] Compt. rend., **108**, 477 (1889).

[2] *Ibid.*, **97**, 96 (1883).

the unstable blue compound of chromic anhydride and hydrogen peroxide, reached the conclusion that it must be represented by the formula H_2CrO_5, or $CrO_3.H_2O_2$.

Similarly, in order to explain the great acceleration caused by small amounts of molybdic and tungstic acids in the oxidation of hydriodic acid by hydrogen peroxide, Brode[1] has been led to assume the formation of permolybdic and pertungstic acids as the result of the action of the peroxide on the catalyzer, and in the same year Camerer obtained complex peracids of molybdenum and tungsten, to which he assigned these formulas, respectively: $2MoO_3.H_2O.H_2O_2$ and $WO_3.$ $H_2O.H_2O_2$. It has also been recently shown by Job[2] that cerous salts can act as oxygen carriers in the presence of hydrogen peroxide, probably through the alternate formation and decomposition of cerium trioxide.

Quite recently Petrenko,[3] while studying the action of hydrogen peroxide on sodium arsenate, obtained a compound having the composition $Na_9As_3O_{17}.21H_2O$. This he found to be a hydrogen peroxide derivative having the following constitution: $3Na_2AsO_4.5H_2O_2.16H_2O$. So also has Kazanesky,[4] obtained the compounds $K_2CO_3.2H_2O_2.\frac{1}{2}H_2O$ and $K_2CO_3.$ $3H_2O_2$. Similarly, Staedel[5] has recently found that on adding a 90 to 95 per cent solution of hydrogen peroxide to a concentrated aqueous solution of cadmium chloride, a compound was obtained which crystallized in silky needles. It was found to contain 23 per cent of hydrogen peroxide, the theoretical for $CdCl_2.2H_2O_2$ being 27.09 per cent.

Jones and Carroll[6] have recently investigated the lowering of the freezing-point of certain salts and acids in aqueous hydrogen peroxide as a solvent. In discussing the abnormal lowering of the freezing-point of certain of these salts, such as potassium nitrate, in this solvent, these observers make this significant statement: '' The most probable explanation of the above results, all things considered, seem to us to be that

[1] Ztschr. phys. Chem., **37,** 257 (1901).
[2] Compt. rend., **134,** 1052 (1902).
[3] J. russ. phys. chem. Soc., **34,** 391 (1902).
[4] *Ibid.*, **34,** 388 (1902).
[5] Ztschr. angew. Chem., **15,** 642 (1902).
[6] This JOURNAL, **28,** 284; see also *Ibid.*, **27, 22** (1902).

there is union between the molecules of the salts investigated and the molecule of hydrogen peroxide.''

There seems to be abundant evidence, therefore, that hydrogen peroxide is not only able to form peroxides, but that it also frequently combines directly with these to form complex, unstable addition-products, and that oxidations by means of this substance are largely, if not entirely, brought about by the formation and subsequent decomposition of these complex compounds. Such being the case, it is believed that we have a simple and intelligible explanation of all oxidations that can be accomplished by this substance :

1. In the oxidation of such substances as sulphurous acid, formic aldehyde, phenolphthalin, and ammonium sulphocyanate, etc., one or more of the molecules of hydrogen peroxide add themselves to these several substances in exactly the proportion required to bring them to their highest labile, holoxide condition of oxidation, the complex derivatives thus produced then breaking down into water and the highest stable oxidation-product of the substance in question. Thus :

(1) $H_2SO_3 + H_2O_2 = H_4SO_5 = H_2SO_4 + H_2O$;

(2) $HCOH + H_2O_2 = H_4CO_3 = HCOOH + H_2O$;

$$(3)\ C \begin{cases} C_6H_4OH \\ C_6H_4OH \\ C_6H_4COOH \\ H \end{cases} + H_2O_2 \quad = \quad C \begin{cases} C_6H_4OH \\ C_6H_4OH \\ C_6H_4COOH \\ H.H_2O_2 \end{cases} =$$

$$C \begin{cases} C_6H_4OH \\ C_2HOH \\ C_6H_4CO \\ O \longrightarrow \end{cases} + 2H_2O\ ;$$

and

$$(4)\ NH_4CNS + 3H_2O = NH_4CNS.3H_2O_2 =$$
$$NH_4HSO_4 + HCN + 2H_2O.$$
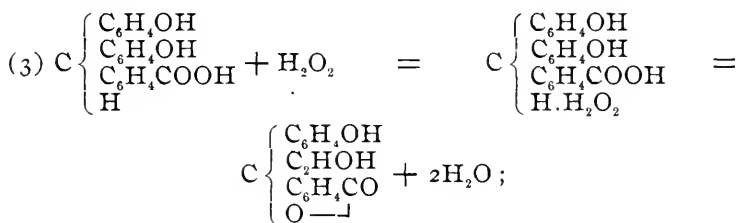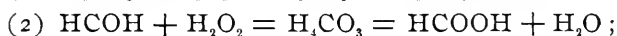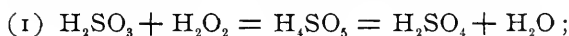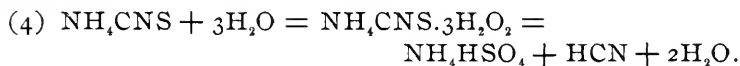
2. It is conceivable that certain substances might combine with a larger amount of hydrogen peroxide than that required to effect their oxidation to the highest stable state, in which event they might act as oxidizing agents toward a second substance, and hence as a carrier of oxygen from hydrogen peroxide to the second substance, or their holoxide derivatives

might undergo decomposition with the evolution of oxygen gas. In this category would naturally fall such an oxidation as that of the nitrils, to which reference has been made above. If R.CN were to unite with 2 molecules of hydrogen peroxide we would have $R.CN.2H_2O_2$. This would then decompose in the sense of this equation :

$$R.CN.2H_2O_2 = R.CONH_2 + H_2O + O_2;$$

or, as a small amount of alkali is necessary to this oxidation, it is probable that the hydrogen peroxide first combines with this to form a compound like that obtained by Schöne, $H_4K_2O_6$, and that this then combines with the nitril, the product of this combination decomposing at once into the amide, water, molecular oxygen, and potassium dioxide, and that this last combines with more peroxide to form $H_4K_2O_6$, and that these changes thereby take place over and over again until all of the nitril is oxidized. This would explain why Radziszewski found that only a drop or two of caustic potash solution was required to completely oxidize a solution of cyanogen to oxamide.

3. This same explanation would seem to hold for the action of oxygen carriers generally on oxidations by means of hydrogen peroxide. Either the carrier is first oxidized to an unstable peroxide condition by the hydrogen peroxide, or it unites directly with it, or both changes may occur, producing in any case a complex holoxide derivative which oxidizes certain substances more readily than hydrogen peroxide alone. On the other hand, this complex holoxide compound may also break down, yielding water, molecular oxygen, and the original carrier, or some stable oxidation-product of the latter. This is in harmony with Schöne's explanation of the catalytic decomposition of hydrogen peroxide by the alkalies and alkaline earths, and we have seen in the preceding paragraph that alkalies act as oxygen carriers in the oxidation of the nitrils by hydrogen peroxide. Further, Manchot has pointed out that the oxygen-carrying power of iron salts in the presence of hydrogen peroxide can best be accounted for on the assumption that a peroxide of iron is produced.

Many reactions exceedingly difficult of explanation thus be-

come readily intelligible in the light of this hypothesis. Take, for example, the action of hydrogen peroxide upon silver oxide and upon metallic silver, concerning which so much has already been written and such widely differing opinions held as to its cause. It is known that silver shows some resemblances to potassium even in the conduct of their oxides. Such being the case, it cannot be far-fetched to assume that when silver or silver oxide is brought into hydrogen peroxide, it is oxidized to Ag_2O_2, and that then the hydrogen peroxide produces with this a higher holoxide derivative, such as $H_4Ag_2O_6$. We know, however, that silver has but little affinity for oxygen, even in the form of argentous oxide. It is not surprising, therefore, that this more complex compound should decompose easily into water, molecular oxygen, and metallic silver.[1] Or perhaps under slightly different conditions, such as a slight difference in the reaction of the solution, this decomposition might result in the formation of a higher oxide of silver, such as Ag_2O_2 or Ag_4O_3, as has been contended by Berthelot.[2] Or if a readily oxidizable substance were present, the silver or silver oxide might act as a carrier of oxygen instead of simply effecting the decomposition of hydrogen peroxide, for the reason that its holoxide derivative would give up part of its oxygen to the oxidizable substance, instead of giving it all up in the form of molecular oxygen. Or both of these processes, namely, the decomposition of the peroxide and the carrying of oxygen, might occur simultaneously. In fact, such is generally the case. The theory here advanced indicates these processes to be correlated phenomena, and the fact that the oxidation of a substance by hydrogen peroxide in the presence of a carrier rarely, if ever, takes place without the decomposition of a portion of the peroxide, is a strong argument in favor of the correctness of this view.

[1] See the work of Baeyer and Villiger on this point. Ber. d. chem. Ges., **34**, 749 (1901).

[2] In opposition to the views of Thénard and those of Baeyer and Villiger concerning the decomposition of hydrogen peroxide by silver oxide, Berthelot contends that silver peroxide is produced as an intermediate product and that it unites with some of the oxide of silver to produce the compound Ag_4O_3. Ann. chim. phys., [7], **11**, 223 (1897).

For a thorough understanding of such reactions, it is well to remember that the tendency to form molecular oxygen is no inconsiderable element in the affinities which are at work to bring about these changes. That such is the case is seen by the fact that the change of ozone into oxygen is an exothermic process, and that in the decomposition of hydrogen peroxide into water and molecular oxygen 22,000 cals. of heat are evolved :

$$2H_2O_2 = 2H_2O + O_2 + 22,000 \text{ cals.}^1$$
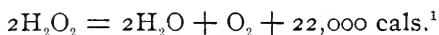
On the other hand, before we can have atomic oxygen available for the purposes of oxidation, it is necessary that energy enter the system either directly or as the result of chemical change. In view of this, and of what has already been given above, there is every reason for supposing that the oxygen evolved in these processes does not result directly from the hydrogen peroxide, but rather indirectly from the decomposition of these complex addition-products of hydrogen peroxide with the oxidizable substance, and that the formation of molecular oxygen as the result of the decomposition of these complex oxygen compounds is essentially similar to the formation of molecular nitrogen from the decomposition of a diazo compound. The ideas here advanced enable us to understand how it is that hydrogen peroxide sometimes acts as an oxidizing agent, without any evolution of oxygen, while under other conditions it oxidizes most rapidly when it is giving off oxygen gas most freely. In the first case, the hydrogen peroxide adds itself to the oxidizable substance to form a labile holoxide derivative, which by rearrangement, and in some instances by splitting off water, furnishes the highest stable oxidation-product of the substance in question. Hence, in such oxidations, no molecular oxygen is evolved. A good example of this mode of action is furnished by the oxidation of sulphur dioxide by hydrogen peroxide. According to our view of the matter, sulphur dioxide combines directly with hydrogen peroxide to form the labilé holoxide derivative $H(O_2)$ $\diagdown$ SO_2, isomeric with sulphuric acid. This compound $H \diagup$

---

[1] Mendeléeff's "Principles of Chemistry," (1897), Vol. I., p. 208, foot-note 18.

then undergoes molecular rearrangement, and forms sulphuric acid with the evolution of heat. Thus:

$$\begin{array}{c} H(O_2) \\ \diagdown \\ H \diagup \end{array} SO_2 \quad = \quad \begin{array}{c} HO \\ \diagdown \\ HO \diagup \end{array} SO_2.$$
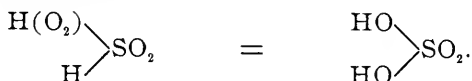
Similarly in the oxidation of formic aldehyde by hydrogen peroxide the following changes would probably occur:

$$(1) \quad \begin{array}{c} H \\ \diagdown \\ H \diagup \end{array} C = O + H_2O_2 = \begin{array}{c} H \\ \diagdown \\ H \diagup \end{array} C \begin{array}{c} \diagup OH \\ \diagdown (O_2)H \end{array} ;$$

and $\quad (2) \quad \begin{array}{c} H \\ \diagdown \\ H \diagup \end{array} C \begin{array}{c} \diagup OH \\ \diagdown (O_2)H \end{array} = HCO.OH + H_2O.$
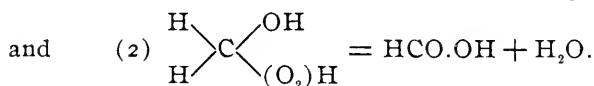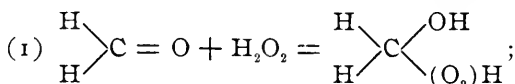
It has also been observed that in those oxidations by the peroxide which are more or less dependent on the presence of finely divided platinum or a similar carrier, the oxidation and the catalysis are both affected alike by temperature. At low temperatures oxygen is given off slowly and the oxidation is correspondingly slow, whereas, at higher temperatures, both the catalytic decomposition and the oxidation are greatly accelerated. This correlation of properties on the part of the carrier and the similar effect of the temperature on the two processes, can be readily understood when it is borne in mind that the formation and decomposition of the unstable oxygen compound produced by the action of the peroxide on the carrier is a function of the temperature, and that at low temperatures it would probably be formed less readily and be more stable than at higher temperatures. Hence, at very low temperatures, hydrogen peroxide would probably not be decomposed by platinum black, nor would the latter induce the oxidation of any substance by the peroxide. On the other hand, at higher temperatures, the unstable peroxide addition-product of the carrier and hydrogen peroxide would not only be produced more rapidly, but would also decompose more easily, and hence would oxidize the reducing substance more rapidly. In this manner the conduct of a carrier like platinum black can be satisfactorily explained.

In an inquiry into the cause of oxygen transmission by

platinum, E. von Meyer[1] decided against de la Rive's hypothesis of alternate oxidation and reduction of the carrier, mainly for the reason that he found PtO, $PtO(OH)_2$, and PtO_2 to conduct themselves differently from spongy platinum and air towards a mixture of hydrogen, carbon dioxide, and oxygen. He, therefore, rather inclined to the view of Hüfner, that the platinum acts by loosening the affinities of the atoms within the oxygen molecule, thus rendering it more active. According to our conception, von Meyer's results are easily explained. It is more than likely that the oxides of platinum, which he compared with a mixture of air and spongy platinum in their oxidizing power towards a mixture of hydrogen and oxygen, are by no means the same as the highly unstable holoxide compound of the metal and oxygen, which is alternately formed and reduced during the oxidation. Indeed the whole modern theory of oxidation rests upon the assumption, well verified in many cases, that it is not the final products of oxidation that are first formed during the process but very unstable holoxides. These intermediate products may carry oxygen to other less oxidizable substances, or react with water to form hydrogen peroxide, or in some cases give off ozone. The formation of ozone in the slow combustion of phosphorus, for example, is inexplicable by any other assumption, and yet the holoxide of phosphorus, which is the precursor of phosphorus pentoxide and ozone, has never been isolated.[2] We do not look to phosphorous or phosphoric oxide, however, to explain the oxygen-carrying power of phosphorus, and why should we do this in the case of platinum? Then again, Hüfner's explanation is no explanation at all. The only means of loosening the affinities of an element is by kinetic energy, or by the combination of the substance with another to form an unstable derivative which can accomplish changes impossible to the original substance.

4. In our opinion it is a mistake to look upon the so-called reductions brought about by hydrogen peroxide as reductions in the ordinary sense. In reality they are probably oxidations, at least in their initial phases. In these processes it is

[1] J. prakt. Chem., [2], **14,** 124 (1876).

[2] Ostwald: Ztschr. phys. Chem., **34,** 248 (1900).

certainly more easily conceivable that the hydrogen peroxide first oxidizes the substance whose reduction it ultimately effects, or perhaps, adds itself to it, and that the complex compound thus produced then breaks up into the final products of the change. Thus, as indicated above, silver oxide is probably oxidized and combines with hydrogen peroxide after the manner of the alkalies, thus :

$$(1)\ Ag_2O + 3H_2O_2 = H_4Ag_2O_6 + H_2O\ ;$$

and $\quad(2)\ H_4Ag_2O_6 = 2Ag + 2H_2O + 2O_2.$
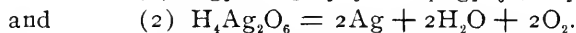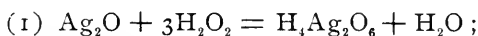
In this same way other so-called reductions by hydrogen peroxide can readily be explained by the supposition that the change is primarily one of oxidation. For example, when lead peroxide and manganese peroxide decompose a neutral or alkaline solution of hydrogen peroxide, the oxygen evolved has been found to come entirely from the hydrogen peroxide, and the metallic peroxides are found unchanged at the end of the process. On the other hand, when they react in an acid solution of hydrogen peroxide, they are reduced and are found at the end of the operation as plumbous and manganous salts.[1] We have seen that the catalytic decomposition of the neutral peroxide can be most simply explained by the supposition that unstable holoxides and hydroholoxides are produced, which by their decomposition give rise to the water, molecular oxygen, and the catalyzer in its original form. Hence, it would seem probable that the reduction of these substances, which is effected in acid solutions of the peroxide, is likewise preceded by the oxidation of the manganese or lead peroxides to more complex holoxide derivatives, and that it is upon the latter that the acid acts, with the production of water, molecular oxygen, and an *-ous* salt of the metal. As a matter of fact, numerous instances are known in which higher and more unstable oxides are more readily acted upon by acids than the corresponding lower and more stable oxides.

Then again, take the action of hydrogen peroxide on an acid solution of potassium permanganate, whereby the permanganate is reduced with the formation of a manganous salt,

[1] Martinon : Bull. soc. chim., **43**, 355 (1885).

water, and molecular oxygen. This reaction has been variously interpreted by different observers. According to Berthelot, and later according to Bach, the permanganic acid oxidizes the hydrogen peroxide to hydrogen trioxide, and this undergoes decomposition into water and molecular oxygen. Here one-half of the oxygen given off is furnished by each of these substances. According to Schönbein, atomic oxygen is given off simultaneously in this process from the hydrogen peroxide and the permanganic acid, forming molecular oxygen, whereas, according to Traube and Weltzien, the permanganic acid oxidizes the hydrogen of the hydrogen peroxide to form water, so that the oxygen evolved in this process really comes entirely from the hydrogen peroxide.

Baeyer and Villiger[1] object to Schönbein's explanation that both of the substances concerned act as oxidizing agents. They even go so far as to say that hydrogen peroxide is scarcely to be considered an oxidizing agent since, in pure state, it decomposes dilute hydriodic acid only very gradually. This is certainly a remarkable view to take of the conduct of hydrogen peroxide in the light of all the facts, and one that is certainly not shared by chemists generally. They also object to the views of Berthelot and Bach, that higher oxides of hydrogen are produced by the oxidation of hydrogen peroxide by permanganic acid, on the ground that it does not rest on a sufficiently broad foundation of fact.[2] They are not prepared, however, to urge the stability of Caro's acid towards permanganic acid as an argument against Berthelot's view.

On the other hand, they incline to the views of Traube and Weltzien as best according with the facts, namely, that in the reaction, the permanganic acid oxidizes the hydrogen of the hydrogen peroxide, and that, therefore, the oxygen evolved comes entirely from the hydrogen peroxide itself, and they go so far as to say that the writers of text-books on elementary chemistry would be justified in adopting this explanation of this change. They have likened the oxidation of hydrogen

[1] Ber. d. chem. Ges., **33**, 2488 (1900).

[2] Quite recently, however, Baeyer and Villiger (Ber. d. chem. Ges., **35**, 3038 (1902)) state that the oxides K_2O_4, etc., are derived from the acid H_2O_4, which they call ozonic acid, and of which they consider ozone the anhydride, thus: $O_3 + H_2O = H_2O_4$. This seems to be nothing more than Bach's hydrogen tetroxide. See Bach: Ber. d. chem. Ges., **35**, 3424 (1902); Cf. Clover: This JOURNAL, **29**, 463 (1903).

peroxide under these conditions to that of hydrogen sulphide, and cite other analogies of hydrogen peroxide to hydrogen sulphide in support of this view.

In our opinion, this analogy rests upon a very uncertain and slender foundation of fact, and even admitting its correctness, it must needs impress us as a little peculiar that, in order to oxidize the hydrogen of hydrogen peroxide to water, the oxygen necessary to effect this oxidation must be supplied from an outside source, when the compound itself contains more oxygen than any other compound, unless it is Bach's hydrogen tetroxide, and when, as is well known, half of this oxygen is readily available for the purposes of oxidation.[1]

The view that hydrogen peroxide could oxidize permanganic acid, seems never to have received much attention at the hands of chemists, and yet, as a matter of fact, we have observed that its conduct as an oxidizing agent can be best explained by the supposition that it converts substances upon which it acts into their holoxide forms. According to Brodie,[2] whose views of oxidations and reductions by hydrogen peroxide were remarkably clear and consistent for his time, the reduction of permanganic acid is probably preceded by an oxidation thus :

$$\text{`` } Mn_4O_7 + 5H_2O_2 = Mn_4O_{12} + 5H_2O \text{ ;''}$$
and $$\text{`` } Mn_4O_{12} = 2Mn_2O + 5O_2.\text{''}$$
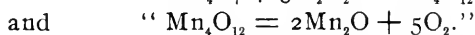
It would seem, therefore, that the simplest view to take of the matter is that the hydrogen peroxide converts permanganic acid into a normal holopermanganic acid, having the composition :
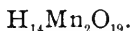
$$H_{14}Mn_2O_{19}.$$

This compound, $H_{14}Mn_2O_{19}$, may be regarded as being derived from the anhydride of permanganic acid, Mn_2O_7, by the combined action of water and hydrogen peroxide.[3] Normal per-

[1] Bach, also, is of the opinion that Traube's view, supported by Baeyer and Villiger, that the peroxide of hydrogen contains easily oxidizable hydrogen, is contrary to reason. Chem. News, **85,** 220 ; Moniteur Scientifique (4) **17,** 26 (1903).

[2] J. Chem. Soc. (London), **17,** 281 (1864).

[3] It has been shown previously by one of us, Kastle, that the composition of a great many hydrates of the metallic nitrates can be satisfactorily explained by the assumption that these complex compounds are derived from normal nitric acid, H_5NO_5, and similar explanations doubtless hold for many other complex compounds now but little understood. This JOURNAL, **20,** 814.

manganic acid is derived from the oxide Mn_2O_7 by the addition of 7 molecules of water, thus :

$$Mn_2O_7 + 7H_2O = H_{14}Mn_2O_{14},$$

and hence must have the formula

$$H_{14}Mn_2O_{14} \text{ or } H_7MnO_7 \text{ or } MnO_{3\,1/2}.3\tfrac{1}{2}H_2O.$$
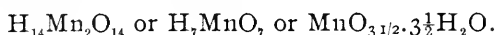
Now assuming that 1 molecule of water enters into the composition of normal holopermanganic acid, and remembering that, in the formation of these addition-products of hydrogen peroxide, the hydrogen peroxide is equivalent to water, it will be observed that 2.5 molecules of hydrogen peroxide will be required to produce normal holopermanganic acid, or for the double formula of permanganic acid 5 molecules of hydrogen peroxide will be required. Now, this is the quantity of peroxide actually required to effect the decomposition of acid permanganate, thus :

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 =$$
$$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$
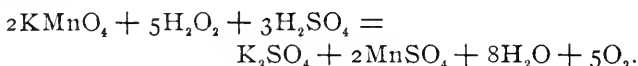
In the light of Berthelot and Bach's observations, however, it is probable that the decomposition of normal holopermanganic acid under the influence of acids takes place more gradually than the above equation would indicate. According to our view of the matter, it would probably take place in this way :

$$H_{14}Mn_2O_{19} = 2Mn(OH)_2 + 5H_2O_3.$$
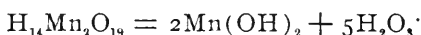
This would satisfactorily explain the formation of the higher oxides of hydrogen, and would account satisfactorily for the fact observed by Berthelot, that a mixture of potassium permanganate, sulphuric acid, and hydrogen peroxide at $-12°$ C. becomes colorless, without the evolution of oxygen.

Baeyer and Villiger observed that oxygen is readily evolved from this cold solution by shaking. They, therefore, looked upon the phenomenon as one of supersaturation. As we know, however, oxygen is only slightly soluble in water, hence it is rather difficult to understand how it could form supersaturated solutions containing such large amounts of oxygen. On the other hand, we know that agitation assists

the decomposition of any very unstable compound; so that these facts are much more easily explained by the supposition that a holopermanganic acid is formed and undergoes decomposition than by any other hypothesis. Another point brought out by Baeyer and Villiger is that Caro's acid, persulphuric acid, is much more stable towards permanganic acid than hydrogen peroxide. They account for this by the supposition that easily oxidizable hydrogen becomes more difficult to oxidize by combination with an acid radical, as may be observed in the conduct of phosphine, hypophosphorous, and phosphorous acids towards oxidizing agents.

On the supposition that normal holopermanganic acid is produced by the action of hydrogen peroxide on permanganic acid, we have a more simple explanation of the greater stability of persulphuric acid towards permanganic acid than any that has hitherto been advanced. According to our hypothesis, persulphuric acid and holopermanganic acid are analogous compounds, both being holoacids. Therefore, there would be but little or no tendency on the part of the former to produce the latter from permanganic acid. On the other hand, we have observed that just as water is primarily an agent which effects hydrolysis, so hydrogen peroxide possesses a marked tendency to oxidize a great variety of compounds to the holoxide condition.

It is highly probable, therefore, that all reductions effected by hydrogen peroxide are always preceded by an oxidation of the substances reduced. In other words, that the reduction is of the nature of a secondary process and often tends to disguise the true significance of the reaction.[1]

[1] Since this communication went to press similar ideas regarding the apparent reduction of certain metallic compounds by hydrogen peroxide have been advanced by Bach. As the result of his study of the action of chromic acid on hydrogen peroxide, he arrived at the conclusion that superoxygenated derivatives of chromium are produced. The formation of such a compound would, according to him, enable us to explain the decomposition of the peroxide by the metallic oxides more or less rich in oxygen, in a very simple manner. In the case of certain elements, such as uranium, vanadium, titanium, molybdenum, etc., etc., these intermediate compounds are relatively stable and can be isolated; in the case of other elements, such as chromium, the intermediate compound is only slightly stable, but its characteristic coloration places its formation beyond all possible doubt. In the case of other elements again, such as silver, platinum, lead, and manganese, the formation of the intermediate compound is not made manifest by any outward sign. Towards the close of his article he says:

Finally, it is believed that the formation of these unstable holoxide derivatives by the action of hydrogen peroxide on various catalyzers, and their subsequent decomposition into molecular oxygen, water, and the catalyzer in its original form, affords a satisfactory explanation of the catalytic decomposition of hydrogen peroxide by these various substances. According to our view of the matter, these unstable holoxide derivatives may react in two ways. They may either effect the oxidation of certain reducing agents, which cannot be oxidized by hydrogen peroxide alone, or, in the event that such reducing agents are not at hand, these holoxide derivatives may undergo decomposition themselves, yielding molecular oxygen, water, and the catalyzer in its original form, or a stable oxidation-product of the latter. The fact that both of these processes take place, as a rule, simultaneously, and that, generally speaking, a good oxygen carrier is also a good catalyzer, and vice versa, is of itself good evidence that these two processes are causally related, and furnishes one of the strongest arguments in favor of the correctness of this view. Additional evidence of its correctness is afforded by the following observations :

1. It has been observed by Kastle and Clark[1] that when hydrogen peroxide is brought in contact with finely divided copper, a certain interval elapses before the decomposition begins. During this latent period the copper undergoes a marked change of color, passing from a dull-red to a dark-brown or black. As soon as this change of color occurs, the decomposition of the hydrogen peroxide begins actively and continues as long as any of the compound is present.

Now, according to our view of the matter, finely divided copper can effect the decomposition of hydrogen peroxide only

"In the presence of acids the intermediate compound undergoes a more decided decomposition with the evolution of oxygen and the formation of a salt. If the oxide employed contains ' disposable ' oxygen, that is to say, oxygen in excess of that required to form a salt with the maximum amount (MnO_2, PbO_2, MnO_4H, CrO_3) this oxygen is given off at the same time as that from the peroxide of hydrogen, which causes the illusion of the simultaneous reduction of the metallic oxidizer and the peroxide of hydrogen. As a matter of fact, there is nothing but the more or less spontaneous decomposition of the superoxygenated product, formed by the fixation of the peroxide of hydrogen on the metallic oxide brought into the reaction." Moniteur Scientifique, [4], **17**, 26. See also Chemical News, **87**, 32.

[1] This JOURNAL, **26**, 526 (1901).

by being first converted into some unstable holoxide deriva-
tive. The formation of such a compound by the action of the
peroxide on the metal is seen in the change of color which the
latter undergoes prior to the decomposition, and the latent
period here observed represents the time interval necessary for
the formation of this unstable compound.[1] There seems to be
no necessity for supposing that these phenomena are peculiar
to copper. On the other hand, there is every reason to be-
lieve that in the decomposition of hydrogen peroxide by other
metals and by various other catalyzers, we have the same suc-
cession of events, the conversion of the catalyzer into the hol-
oxide form, followed by its decomposition into molecular oxy-
gen, water, and the catalyzer, the only difference being that
this succession of events takes place more rapidly with most
catalyzers than with copper, and without a change of color in
most cases.

THE RÔLE OF CATALASE IN THE LIVING CELL.

It was long ago pointed out by Schönbein that one of the
most characteristic and universal properties of living proto-
plasm is its power to decompose hydrogen peroxide. Indeed,
he looked upon this decomposition as the prototype of all fer-
mentative activity, and gradually it came to be accepted as a
fact that all ferments and enzymes possess this property in com-
mon, and correlated with it, the power also to give the guaia-
cum reaction in the presence of hydrogen peroxide. Strange
to say, these ideas still find a place in the recent literature of
the subject.

On the other hand, in 1888, Bergengrün[2] found that fibrin
ferment does not decompose hydrogen peroxide, and in 1892

[1] In order to explain the period of induction observed in the combination of moist
hydrogen and chlorine, a number of observers have found it necessary to assume
the formation of an intermediate compound. Recently Mellor, in a remarkably
accurate and painstaking investigation, has shown that this intermediate compound
is not Cl_2O or $HClO$, but a substance the composition of which he represents by the
formula $xCl_2.yH_2O.zH_2$, where $x, y,$ and z are positive integers. If we assume the
existence of such an intermediate compound, then, according to him, the period of
induction is a necessary consequence of the law of mass action. J. Chem. Soc. (Lon-
don), 81, 1292 (1902).

[2] Ueber die Wechselwirkung zwischen Wasserstoffsuperoxyd und verschiedenen
Protoplasma Formen, Dorpat, 1888. Cited by Loew: Report No. 68 U. S. Department
of Agriculture (1901).

Jacobson[1] observed that by carefully heating emulsin it might be made to lose its power to decompose hydrogen peroxide, without losing its power to hydrolyze amygdalin. It might also be noted in passing that very powerful preparations of certain enzymes have been on the market for a long time, which have but very feeble action on hydrogen peroxide.

In 1897 Spitzer[2] pointed out that the power to decompose hydrogen peroxide is due to one enzyme only, *viz.*, to that which gives the guaiacum reaction. It has been observed by Loew,[3] however, that, while aqueous extracts of cured tobacco have the power of actively decomposing hydrogen peroxide, they did not have the power to hydrolyze albumin, starch, cane-sugar, or amygdalin, and also that such extracts were unable to give the guaiacum reaction, even in the presence of hydrogen peroxide. He therefore reached the conclusion that the power of various animal and plant extracts to decompose hydrogen peroxide is due to a distinct enzyme of general occurrence, to which he gave the name of "catalase." Naturally there has been considerable speculation as to the physiological rôle of catalase in the cell. Schönbein connected it with the process of respiration, *i. e.*, with oxidations occurring in the organism, and in harmony with this idea, Spitzer later reached the conclusion that the power of a given tissue to decompose hydrogen peroxide is a true index of its oxidizing power. On the other hand, it was afterwards shown by Lépinois[4] that for the various tissues there does not always exist this parallelism between the quantities of oxygen evolved from hydrogen peroxide as the result of their action and the intensity of their other reactions, such as the oxidation of guaiacum, guaiacol, etc. Therefore, in attempting to explain the rôle of catalase in the living cell, Loew has found it necessary to depart somewhat from formerly accepted ideas as to its physiological significance. According to this observer, catalase may act beneficially in the cell in three ways :

1. On the supposition that hydrogen peroxide is a constant

1 Ztschr. physiol. Chem., **16**, 340 (1892).
2 Pflüg. Arch., **67**, 615 (1897).
3 U. S. Dept. of Agr., Report No. 68 (1901).
4 Compt. rend. Soc. Biol., 1899, p. 401.

by-product of all respiratory processes, he assumes that the chief function of catalase is to destroy this substance as fast as found, thereby protecting the cell against toxic action.

2. In view of the fact that catalase is found in anaerobic micro-organisms, in which hydrogen peroxide is not produced, he assumes that this enzyme has the property of loosening the affinities in certain other compounds besides hydrogen per-oxide, in order that the protoplasm may be able to effect their decomposition more easily. " In other words," he says, " catalase might represent an aid for fermentative as well as for respiratory phenomena." [1]

3. He suggests that catalase may be able to effect certain reductions, since platinum-black can bring about both oxida-tions and reductions.

It seems to us that the first suggestion of Loew's, that the chief physiological rôle of catalase is to prevent the accumulation of hydrogen peroxide in the cell, is highly improbable. In the first place, Erlenmeyer's hypothesis that hydrogen peroxide is produced as a by-product in the assimila-tion of carbon dioxide by green plants is as yet entirely with-out experimental proof, and it certainly cannot be said to have been proved conclusively that hydrogen peroxide is present either in vegetable or animal tissues, although this in itself would really be no argument against Loew's hypothesis.

As a matter of fact, if hydrogen peroxide is produced at all in respiratory processes, it can only result from the interac-tion of organic peroxides (oxidases) with water and basic substances. We have endeavored to prove in a former com-munication[2] that the so-called oxidases are probably nothing more than unstable organic peroxides, which are produced in the cell as the first oxidation-products of certain autoxidizable substances, and this view is shared by Bach and others. Now, as is well known, these unstable peroxides can either oxidize a second molecule of the substance from which they are derived, or any other strongly reducing substance that may happen to be present. That such is the case is evident from the work of Baeyer and Villiger on the oxidation of benzalde-

[1] *Loc. cit.*, p. 44.
[2] This JOURNAL, **26**, 539 (1901).

hyde.[1] According to these observers, this compound may participate in the following changes :

(1) $C_6H_5CHO + O_2 = C_6H_5CO.O.OH$

and (2) $C_6H_5CO.O.OH + C_6H_5CHO = 2C_6H_5COOH$,

or (3) $C_6H_5CO.O.OH + indigo = C_6H_5COOH + isatin.$
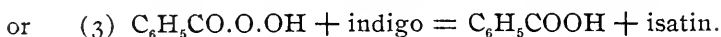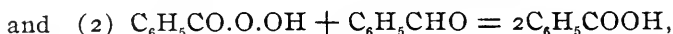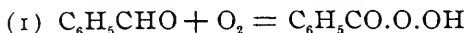
The organic peroxides or oxidases would, therefore, only react with water, or a basic substance, to form hydrogen peroxide, in case no further quantities of reducing substances were present, and this under normal conditions of life and growth is exceedingly improbable.

Even supposing that small amounts of hydrogen peroxide should be produced by the action of water on the organic peroxides, it is known that associated with catalase there are enzymes or substances present in the animal and plant cell which can act as oxygen carriers and enable the hydrogen peroxide thus produced to effect certain oxidations. This is evident from the so-called peroxidase reactions. An extract of liver, for example, does not oxidize either guaiacum or phenolphthalin directly, but in the presence of hydrogen peroxide both of these substances are oxidized, and at the same time the hydrogen peroxide is rapidly decomposed. Hence it is more than probable that even if hydrogen peroxide were produced in the cell, it would be at once turned to account for the process of oxidation.

Finally, even admitting that hydrogen peroxide should be produced in the cell as the result of any of these reactions, and that it could not be turned to account in the manner indicated, it is still difficult to conceive that the rôle of catalase should be to destroy this substance as a safeguard against its toxic action, when, keeping in mind the peroxide nature of the oxidases, we remember that, as has been recently shown by Freer and Novy,[2] the organic peroxides, particularly of the asymmetrical type, are much more powerful antiseptics than hydrogen peroxide itself. Certainly all of these facts should be taken into account, and if they are, it is hardly conceiva-

[1] Ber. d. chem. Ges., **33**, 1569 (1900).
[2] This JOURNAL, **27**, 161 (1902).

ble that the chief rôle of catalase in the cell is to destroy hydrogen peroxide.

On the other hand, the fact that the two modifications of catalase, in the absence of other oxidases, can oxidize hydroquinone, as has been proved by Loew, would seem to indicate that catalase is really an oxidase.   This is in harmony with the fact that most, if not all, substances which can break down hydrogen peroxide, can also effect the oxidation of various substances in contact with molecular oxygen.   Platinumblack, other finely divided metals, and bone-black are substances of this kind.

In this connection it should also be borne in mind, as has been pointed out above, that those substances which are able to effect the decomposition of hydrogen peroxide, can also, under suitable conditions, act as oxygen carriers in the oxidation of various substances by the peroxide.   Apparently catalase is an exceptional catalyzer, in the sense that while it readily decomposes the peroxide, it, according to Loew, is incapable of transmitting oxygen from the peroxide to guaiacum.   In other words, catalase, when free from other enzymes, does not give the peroxidase reactions.

In spite of its exceptional conduct in this respect, and in the light of Loew's result showing that catalase can oxidize hydroquinone, we are inclined to Schönbein's view that the substances in the living cell which are capable of effecting the decomposition of hydrogen peroxide, are concerned in some way with oxidation phenomena, that is, if these substances have any physiological rôle at all.

From the facts as they are known to us at present, it would seem most logical to look upon catalase as a substance or mixture of substances capable of combining with oxygen to form an oxidase, and with hydrogen peroxide to form an unstable holoxide derivative.   This would explain its oxidizing action on hydroquinone and at the same time would offer a satisfactory explanation of its power to decompose hydrogen peroxide, and would put it in the same class with other hydrogen peroxide catalyzers.   The fact that it does not oxidize guaiacum in the presence of hydrogen peroxide is not surprising

when we recall the specific character of the oxidations brought about by oxidases. Tyrosinase, for example, will oxidize tyrosine, but not salicylic aldehyde, and aldehydase will oxidize salicylic aldehyde, but not tyrosine. In other words, a number of oxidizing ferments are known which seem to be specific in their oxygen-carrying powers. It should also be borne in mind in this connection that both Aso[1] and Bach,[2] independently, have reached the conclusion that at least two peroxidases occur in plants.

From our standpoint, therefore, the power possessed by catalase to decompose hydrogen peroxide is to be looked upon, not as its physiological function, but rather as a property possessed in common by a great many substances capable of combining with oxygen, a property, by the way, which may never be called into play physiologically.

The idea that probably catalase is a reducing substance is shared by others, and by Loew himself. Recently Pozzi-Escot[3] has shown that, in most respects at least, it is identical with the "philothion" of de Rey-Pailhade. As is well known, this last-named substance belongs to that class of soluble ferments known as the reductases.

Now, according to de Rey-Pailhade[4], philothion should be able to combine with oxygen as well as with sulphur, and this, according to him, is its principal function. Pozzi-Escot has pointed out that the action of philothion or catalase on hydrogen peroxide is not strictly catalytic, but that it at length ceases, owing to the oxidation of the substance. This is just what we should expect if our view of the nature and function of catalase is correct.

Summary of Results.

The results and conclusions reached in this investigation may be briefly summarized as follows :

1. It has been found that in many instances at least the inhibition of the catalytic decomposition of hydrogen peroxide by various metals is due to the formation of thin, insoluble,

---

[1] Bulletin College of Agriculture, Tokyo, 5, 2, 218 (1902).

[2] Ber. d. chem. Ges., **36**, 605 (1903).

[3] Bull. soc. chim., [3], **27**, 280 (1902) ; This JOURNAL, **29**, 552 (1903).

[4] Compt. rend., **106**, 1683 ; **107**, 43 (1888) ; **108**, 356 (1889).

protective films over the surface of the metal, the formation of which is brought about by the action of the inhibitor on the metal. In our opinion the inhibitory effect of these substances, many of which happen to be poisons, in nowise indicates any real analogy between the finely divided metals and the soluble ferments. In our opinion, therefore, the use of the term "platinum poison" in this connection, is altogether misleading and fallacious.

2. It has also been pointed out that, during the decomposition of hydrogen peroxide by various catalyzers, we have no evidence of the formation of atomic oxygen. It has been found, however, that various catalyzers act as oxygen carriers in the presence of hydrogen peroxide, and that, with the exception of catalase, all substances which break down hydrogen peroxide also act as oxygen carriers, and *vice versa*, and that for any given catalyzer the oxidation is proportional to the rate of catalytic decomposition.

From these facts, supported also by much collateral evidence, we have been led to conclude that these two properties, *i. e.*, that of inducing oxidation by hydrogen peroxide and that of effecting its catalytic decomposition, are correlated, and that both depend on the fact that the catalytic agent is capable of reacting or combining with the hydrogen peroxide to form complex unstable holoxide derivatives as intermediate products. In the presence of suitable reducing substances these unstable holoxide derivatives may act as oxidizing agents, or, in the absence of the same, they may undergo spontaneous decomposition into molecular oxygen, water, and the catalyzer in its original form, or an oxidation-product thereof, or, as happens in most cases, if suitable reducing substances are present, both oxidation by the holoxide derivative and its spontaneous decomposition may occur simultaneously.

In keeping with these views, the idea has been advanced that the so-called reductions by means of hydrogen peroxide are always preceded by oxidations, and that in the strict sense of the term hydrogen peroxide is not a reducing agent at all.

3. In the light of these conclusions it would seem that the

physiological function of Loew's catalase is not to effect the
decomposition of hydrogen peroxide as a means of protecting
the cell against the toxic action of this substance, but rather
that catalase is a substance or mixture of substances having
a tendency to combine with hydrogen peroxide to form a very
unstable holoxide derivative, which immediately decomposes
with the evolution of molecular oxygen in the manner above
described for other holoxides. We would not confuse this
property, however, with its physiological function. Rather
are we inclined to look upon catalase as a reducing substance,
which may under some conditions combine with atmospheric
oxygen to form an oxidase,[1] or as Pozzi-Escot[2] has pointed out,
a substance probably identical with de Rey-Pailhade's philo-
thion, which, under certain conditions, can effect reductions.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KY., Nov., 1902.

ON SODIUM PHENYL AND THE ACTION OF SODIUM ON KETONES.

BY S. F. ACREE.

The following work was undertaken at the suggestion and
under the direction of Dr. J. U. Nef. Its object was to pre-
pare sodium phenyl and to ascertain whether it is formed as
an intermediate product in various reactions in which brom-
benzene and sodium are used. Nef came to the conclusion,
from his experiments with sodium phenylacetylene, that
sodium phenyl must first be formed in every case,[3]

$$C_6H_5Br + Na_2 = C_6H_5-Na + NaBr,$$
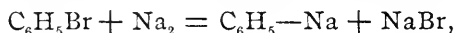
and that this substance subsequently reacts with other re-
agents that may be present, as alkyl haloids (Fittig), ketones
(Frey),[4] carbon dioxide (Kekulé), chlorcarbonic ether
(Wurtz).

We have since succeeded in preparing sodium phenyl from
mercury phenyl and sodium. It reacts with alkyl, aryl, and

[1] U. S. Dept. of Agr., Rep. No. 68, 39-40.
[2] Bull. soc. chim., [3], 27, 280 (1902); This JOURNAL, 29, 552 (1903).
[3] Nef : Ann. Chem. (Liebig), 308, 281, 291.
[4] Frey : Ber. d. chem. Ges., 28, 2514.

acyl halides, with ketones and other reagents, giving practically the same products which are formed when these reagents are treated in ethereal solution with brombenzene and sodium; hence it may be concluded that in those reactions where brombenzene and sodium are used (Fittig's, Frey's, Kekulé's, Wurtz's reactions), sodium phenyl is the intermediate product.

Nef has shown[1] that the reactions of the primary and secondary alkyl haloids with other substances such as alcoholates, amines, etc., depend upon the dissociation of the alkyl haloid into alkylidene and halogen hydride. The halogen hydride is neutralized by the alcoholate, amine, etc., while the alkylidene absorbs the alcohol, amine, etc., that is present, by addition (alkylation). In some cases the alkylidene may also, in part, rearrange to an olefine or polymerize to a dialkylidene.

Sodium phenyl should, from this point of view, interact with primary and secondary alkyl haloids, *e. g.*, ethyl iodide, as follows:

I. $2C_6H_5—Na + 2C_2H_5I = 2C_6H_5—Na + 2CH_3CH + 2HI;$

II. $CH_3CH + Na—C_6H_5$ or $H—C_6H_5 =$
$$CH_3CH—C_6H_5 \text{ or } CH_3CH_2C_6H_5 ;$$
$$\overset{\bullet}{N}a$$

III. $Na—C_6H_5 + HI$ or $CH_3CHNaC_6H_5 + HI =$
$$C_6H_6 \text{ or } C_6H_5CH_2CH_3 + NaI.$$
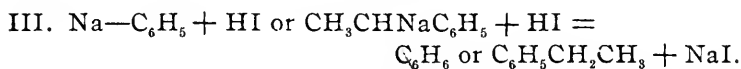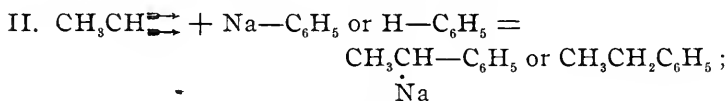
Part of the ethylidene may also go over into ethylene by intramolecular alkylation, or in the case of benzyl chloride the phenylmethylene may polymerize in part to stilbene.[2]

These expectations were in every way realized. It is surprising with what intense violence the interactions of sodium phenyl take place even with an inactive substance like brombenzene.

Preparation of Sodium Phenyl.

When mercury diphenyl is dissolved in dry benzene or ligroin and treated in a flask with a return-condenser, with

[1] Aun. Chem. (Liebig), **309**, 126, **318**, 2.
[2] Nef : *Loc. cit.*

considerably more than the molecular quantity of fine sodium wire, the sodium reacts vigorously with the mercury diphenyl. Sodium amalgam is formed and falls to the bottom of the flask, while a light-brown powder, sodium phenyl, remains suspended in the solution. The larger the amount of sodium used, the more nearly complete is the reaction,

$$Hg(C_6H_5)_2 + 2Na_2 = HgNa_2 + 2NaC_6H_5.$$
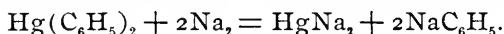
That this powder is sodium phenyl and not sodium mercury phenyl, corresponding to sodium zinc ethyl,[1] was proved by analysis. One sample was made up especially for analysis, as follows: Five grams of mercury diphenyl, dissolved in 100 cc. of benzene, were boiled with five grams of sodium wire until the reaction was complete. Upon adding 2 grams of sodium wire and boiling again there was hardly any action. This showed that very little mercury diphenyl had failed to react with the first portion of sodium. As sodium phenyl is very readily decomposed by the moisture of the air, the analysis was accomplished as follows: A 50 cc. dropping-bottle was fitted with a stop-cock and a stream of dry hydrogen was passed through the bottle; it was then weighed. Part of the sodium phenyl, together with some benzene, was withdrawn from the flask by means of a pipette and transferred to the dropping-bottle. The benzene was then distilled from the dropping-bottle in a stream of hydrogen, leaving behind the sodium phenyl as a dry powder. The dropping-bottle was again weighed, the difference between the two weights giving the amount of the sodium phenyl. When water was added to the dropping-bottle the sodium phenyl was decomposed, forming sodium hydroxide and benzene. The sodium hydroxide was titrated with $N/1$ sulphuric acid and phenolphthalein. There was a small amount of mercury diphenyl, insoluble in water, left in the dropping-bottle. This showed that the sodium phenyl was not quite pure, and accounts for the low results obtained in the analyses.

Analysis of first preparation:

I. 0.5793 gram substance required 5.70 cc. $N/1$ sulphuric acid.

[1] Wanklyn: Ann. Chem. (Liebig), **108**, 67; Z, 1866, p. 253.

II. 0.4329 gram substance required 4.20 cc. N/1 sulphuric acid.

	Calculated for NaC₆H₅.	I.	II.
		Found.	
Na	23.04	22.68	22.36

Analysis of other preparations:

I. 0.3525 gram substance required 3.07 cc. N/1 sulphuric acid.

II. 0.6843 gram substance required 6.47 cc. N/1 sulphuric acid.

	Calculated for NaC₆H₅.	I.	II.
		Found.	
Na	23.04	20.07	21.79

As sodium mercury phenyl, $NaC_6H_5-Hg(C_6H_5)_2$, has only 5.07 per cent of sodium, the above analyses show beyond doubt that the powder is sodium phenyl containing traces of mercury diphenyl. When sodium phenyl is exposed to the air on a filter-paper for a short time, it catches fire. As it is decomposed by water, the reactions were always carried out in the flask in which the sodium phenyl had been prepared, a calcium chloride tube being connected with the flask to prevent access of moisture.

Action of Sodium Phenyl on Ethyl Bromide and on Ethyl Iodide.

By carefully fractionating some low-boiling ligroin a product was obtained that boiled between 54° and 63°. 4.5 grams of mercury diphenyl were dissolved in about 50 cc. of this ligroin and converted into sodium phenyl in the usual way. The flask was then fitted with a dropping-funnel and connected with bromine absorption-tubes to absorb any ethylene formed. 2.5 grams of ethyl bromide were then added slowly through the dropping-funnel, the flask being kept cold by a freezing-mixture. The solution was then warmed to 40° to drive off any ethylene. On treating the bromine in the absorption-tubes with sodium hydroxide a few drops of ethylene dibromide, boiling at about 130°, were obtained. The ligroin solution was very carefully fractionated. After the main portion had distilled over there was a fraction at 80° to 90°, indicating that benzene was present, but this was not proved. The re-

mainder, by repeated fractionation, gave 2 grams of ethyl-benzene, boiling at 130° to 135°. It was treated with nitric acid (20 per cent) in a sealed tube, at 160°, for six hours, and when the tube was opened a great deal of gas escaped. Not all of the ethylbenzene had been decomposed, but 0.5 gram of benzoic acid, melting at 119°, was obtained.

Sodium phenyl and ethyl bromide give, therefore, ethyl-benzene and small amounts of benzene and ethylene.

Sodium phenyl (5 grams) suspended in ligroin (boiling-point 35° to 40°) was treated with the molecular quantity of ethyl iodide in absolute ether, the flask being kept cold. The flask was then connected with bromine absorption-tubes and warmed. Upon treating the bromine with sodium hydroxide only a drop or two of ethylene dibromide remained. When the ligroin solution was fractionated, 2 grams of ethylbenzene, boiling at 130° to 135°, were obtained. Heated with nitric acid, of sp. gr. 1.30, in a sealed tube for six hours at 160°, it gave 1.1 grams of pure benzoic acid melting at 122°.

Action of Sodium Phenyl on Isoamyl Iodide.

Sodium phenyl (5 grams) prepared in ligroin (boiling-point 55° to 60°) was treated with the molecular quantity of iso-amyl iodide in absolute ether, the flask being well cooled by a freezing-mixture. When the reaction was over, the flask was connected with a bromine absorption-apparatus and warmed for some time. The bromine was treated with sodium hydroxide, and 1.1 grams of isoamylene dibromide, of boiling-point 62° to 64° at 15 mm., were obtained. When the ligroin filtrate was distilled a fraction boiling between 80° and 90° was obtained, indicating the formation of benzene in the reaction. Three grams of oil boiling between 175° and 200° were also obtained. This, by refractionation, gave 2 grams of isoamyl-benzene, boiling at 190° to 195° (mostly at 193°).

Sodium phenyl and isoamyl iodide, therefore, give benzene, isoamylene, and isoamylbenzene.

Analysis of isoamylene dibromide :

0.8014 gram substance gave 1.3095 gram AgBr by Carius' method.

	Calculated for $C_5H_{10}Br_2$.	Found.
Br	69.56	69.53

Analysis of isoamylbenzene :

0.2710 gram substance gave 0.8817 gram CO_2 and 0.2658 gram H_2O.

	Calculated for $C_{11}H_{16}$.	Found.
C	89.09	88.73
H	10.91	10.90

Action of Sodium Phenyl on Benzyl Chloride.

When 5 grams of sodium phenyl, prepared in ligroin (boiling-point 55° to 60°), were treated with the molecular quantity of benzyl chloride there was a vigorous reaction. The ligroin filtrate gave, on distillation, 1 gram of a substance having the boiling-point 250° to 270° (diphenylmethane). At 300° to 320° a fraction passed over, which partly solidified. When dried, this melted between 115° and 125° and was shown to be stilbene by its conversion into stilbene dibromide (0.5 gram, melting-point 237°, being obtained). On refractionation, 0.8 gram of diphenylmethane, boiling at 260° to 265°, was obtained, which had the characteristic odor of this substance and which solidified when cooled.

Sodium phenyl and benzyl chloride, therefore, give diphenylmethane and stilbene.

Analysis of diphenylmethane :

0.2230 gram substance gave 0.7584 gram CO_2 and 0.1496 gram H_2O.

	Calculated for $C_{13}H_{12}$.	Found.
C	92.80	92.76
H	7.20	7.45

Action of Sodium Phenyl on Brombenzene.

Sodium phenyl (5 grams) prepared in ligroin (boiling-point 60° to 80°) was treated with 7 grams (1 molecule) of brombenzene in ether. As the reaction was very vigorous, the flask was kept cool by a freezing-mixture. The solution, when distilled, gave 1.1 grams of diphenyl, boiling at 250° to 260°. This solidified and melted at 69° to 70°. Mixed with

a sample of Kahlbaum's diphenyl the melting-point was not lowered. There was a considerable fraction above 300°, but it was a resinous liquid that would not solidify.

Analysis:

0.2397 gram substance gave 0.8203 gram CO_2 and 0.1410 gram H_2O.

	Calculated for $C_{12}H_{10}$.	Found.
C	93.45	93.33
H	6.55	6.54

Action of Sodium Phenyl on Benzophenone.

Frey[1] found that when benzophenone is treated with molecular quantities of brombenzene and sodium in absolute ether, a quantitative yield of triphenylcarbinol is obtained. This has been confirmed. Similar carbinols are obtained when homologues of benzophenone and brombenzene are treated with sodium in the same way. Nef[2] explained this reaction on the basis of an intermediate formation of sodium phenyl, which is subsequently absorbed by the ketone, forming the sodium salt of the carbinol.

$$R{-}Na + R_2C{=}O \longrightarrow R_3{\equiv}CONa.$$

This is proved by what follows :

Mercury diphenyl (5 grams) was treated with sodium wire (5 grams) in benzene, and then 2 grams of solid benzophenone were slowly added with constant shaking and cooling. The mixture was treated with water and sodium carbonate, and the benzene solution then dehydrated and distilled. A residue was obtained which, when recrystallized from ligroin, gave 2.5 grams of triphenylcarbinol, melting at 162°. The ligroin filtrate was evaporated and the residue was digested with phenylhydrazine and absolute alcohol, 0.25 gram of benzophenonephenylhydrazone (melting-point 130°) being obtained. This shows that not all of the benzophenone had been acted upon by the sodium phenyl. A small amount of benzoic acid was obtained by acidifying the sodium carbonate solution. Two grams of benzophenone should give 2.86

[1] Frey : Ber. d. chem. Ges., **28**, 2514.
[2] Nef : Ann. Chem. (Liebig), **308**, 291.

grams of triphenylcarbinol. When we take into considera-
tion the small amount of recovered benzophenone and the
benzoic acid, the yield of triphenylcarbinol actually obtained,
2.5 grams, is nearly quantitative.

Analysis :

0.2382 gram substance gave 0.7644 gram CO_2 and 0.1357
gram H_2O.

	Calculated for $C_{19}H_{16}O$.	Found.
C	87.62	87.52
H	6.21	6.33

The Action of Brombenzene and Sodium on Benzpinacone.

Benzpinacone (5 grams) in absolute ether was allowed to
stand fourteen hours, in a sealed vessel, with 2.5 grams of
brombenzene (1 molecule) and 1 gram of fine sodium wire (1
molecule). The reaction-product was poured into water and
treated with sodium carbonate, but no benzoic acid was found
in the alkaline solution. When the ether was evaporated
and the residue recrystallized from alcohol, 2.4 grams of tri-
phenylcarbinol, melting at 158°, were obtained. On adding
water to the alcoholic filtrate a precipitate of benzhydrol was
obtained, which, when recrystallized from ligroin, weighed
2.2 grams. It melted at 67° and gave a blood-red color with
concentrated sulphuric acid. Benzpinacone is known to dis-
sociate completely into benzophenone and benzhydrol at its
melting-point, 185°, or on heating with alcoholic potash.[1]
The above experiment shows that this dissociation takes place
at room temperature. As fast as benzophenone is formed it
reacts with the sodium phenyl (from brombenzene and so-
dium), giving triphenylcarbinol.

Analysis of benzhydrol :

0.2542 gram substance gave 0.7908 gram CO_2 and 0.1494
gram H_2O.

	Calculated for $C_{13}H_{12}O$.	Found.
C	84.73	84.84
H	6.58	6.53

[1] Thörner and Zincke : Ber. d. chem. Ges., **10**, 1474.

Action of Sodium Phenyl on Benzoyl Chloride.

Mercury diphenyl (4.5 grams) was converted into sodium phenyl in benzene and treated with 1.5 grams of redistilled benzoyl chloride dissolved in absolute ether. The reaction was very vigorous. The mixture was poured into water and extracted with sodium carbonate, but very little benzoic acid was obtained. The benzene was distilled off. The residue, when recrystallized from alcohol, gave 1.5 grams of triphenyl-carbinol melting at 156°. The alcoholic filtrate was boiled with phenylhydrazine, but no benzophenonephenylhydrazone was obtained. This shows that the benzophenone first formed from the benzoyl chloride and sodium phenyl, according to the equation,

$$C_6H_5\underset{\underset{Cl}{|}}{\overset{\overset{O\rightarrow}{|}}{C}}\rightarrow + \overset{\overset{Na}{|}}{C_6H_5} \rightarrow C_6H_5\underset{\underset{Cl}{|}}{\overset{\overset{ONa}{|}}{C}}-C_6H_5 \rightarrow (C_6H_5)_2CO + NaCl,$$
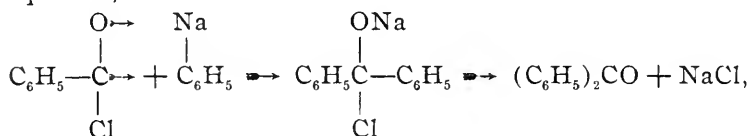
reacts immediately with more sodium phenyl, giving tri-phenylcarbinol.

Action of Sodium Phenyl, and of Brombenzene and Sodium, on Benzil.

Eight grams of mercury diphenyl were converted into sodium phenyl in ligroin (boiling-point 60° to 80°) solution. Solid benzil (5 grams, melting-point 96°) was slowly added with constant stirring and cooling. The reaction took place instantly, a beautiful violet-colored solid being formed. The mass was poured into water, extracted with sodium carbonate, and the ligroin solution was dried with calcium chloride and distilled on a water-bath. When acidified, the sodium carbonate extract gave 1.5 grams of benzoic acid, which melted at 121° when recrystallized. The residue from the ligroin was treated with cold absolute alcohol ; no residue of benz-pinacone was left. The residue obtained by evaporating the alcohol consisted of a mixture of phenylbenzoin,[1]

$$(C_6H_5)_2\overset{\overset{OH}{|}}{C}-CO-C_6H_5,$$
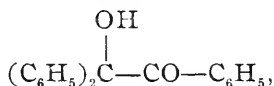
[1] This compound has since been described by Biltz in Ber. d. chem. Ges., **32**, 650 ; see also Nef : Ann. Chem. (Liebig), **308**, 291.

and triphenylcarbinol. These are readily separated by fractional crystallization from ligroin (boiling-point 60° to 80°) or alcohol, in which solvents the phenylbenzoin is by far the more soluble. Thus 1.5 grams of phenylbenzoin, melting-point 84°, and 1.3 grams of triphenylcarbinol, melting-point 155°, were obtained, besides a considerable amount of a resinous product that could not be made to crystallize.

The same products were obtained when benzil was treated with brombenzene and sodium in absolute ether. To 5 grams of benzil in absolute ether were added 4 grams (1 molecule) of brombenzene and 1 gram (1 molecule) of fine sodium wire. The mixture was then kept sealed and cold for three days. The sodium was gradually attacked, an intensely colored, violet-blue solid being formed. Upon pouring the entire mixture into very dilute sulphuric acid, the blue color disappeared immediately. The ethereal solution was extracted with sodium carbonate, and 1 gram of benzoic acid, melting-point 119°, was obtained by acidifying the sodium carbonate solution. When the ethereal solution was dehydrated and distilled, a mixture of phenylbenzoin and triphenylcarbinol remained. This was extracted with ligroin (boiling-point 60° to 80°) and a residue of triphenylcarbinol was left, which, when recrystallized from alcohol, gave 1.2 grams of this substance, melting at 158°. From the ligroin extracts 1.4 grams of phenylbenzoin, melting-point 83°, were obtained.

Brombenzene and sodium, then, react with benzil exactly as sodium phenyl does, giving relatively the same yields of phenylbenzoin, triphenylcarbinol, and benzoic acid.

$$\text{OH}$$
$$|$$
Phenylbenzoin, $(C_6H_5)_2{=}C{-}CO{-}C_6H_5$.
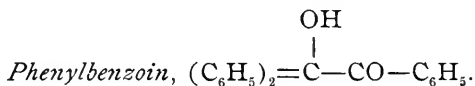
Phenylbenzoin is insoluble in water, but readily soluble in ether, alcohol, and hot ligroin. It crystallizes from the last solvent in radiating needles which melt at 87°. When the substance was dissolved in three parts of 25 per cent methyl alcoholic potash and warmed, a precipitate of potassium benzoate appeared in a short time. This was filtered off and converted into free benzoic acid, melting at 122°. The alcoholic filtrate gave, on addition of water, a white precipitate of benz-

hydrol, melting, when purified from ligroin, at 67°, and giving a blood-red color when warmed with concentrated sulphuric acid. The decomposition of phenylbenzoin by the action of the alkali may be represented as follows:

$$(C_6H_5)_2 : C\underset{COC_6H_5}{\overset{OH}{\diagdown}} + HOK \longrightarrow$$

$$(C_6H_5)_2CHOH + KOCOC_6H_5.$$
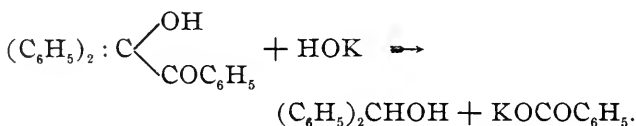
A blood-red color is observed when a solution of phenylbenzoin in concentrated sulphuric acid is warmed. This is also noticed in the case of benzilic acid, benzhydrol, etc., indicating dissociation into diphenylmethylene[1] and other products. The following experiment confirms this view: Phenylbenzoin (0.5 gram) was heated to 240° in a long tube, in a stream of oxygen, for three hours. When cooled, the residue was treated with ether, and there remained a small amount of tetraphenylethylene, melting at 210° to 215°. On extracting the ethereal solution with sodium carbonate and acidifying the alkaline solution, 0.2 gram of benzoic acid, melting-point 120°, was obtained. After distilling off the ether the residue was digested for three hours with phenylhydrazine and alcohol; 0.25 gram of benzophenonephenylhydrazone, melting at 135°, was obtained. The melting-point remained unchanged when it was mixed with a sample of the substance prepared from benzophenone and phenylhydrazine.

Analysis of the phenylbenzoin:

0.2040 gram substance gave 0.6224 gram CO_2 and 0.0992 gram H_2O.

	Calculated for $C_{20}H_{16}O_2$.	Found.
C	83.28	83.21
H	5.60	5.40

The action of sodium phenyl on benzil might result in the formation of two products, phenylbenzoin and benzpinacone, the course of the reaction depending upon whether 1 molecule of benzil reacts with 1 or 2 molecules of sodium phenyl.

[1] Nef : Ann. Chem. (Liebig), **298**, 241.

I. $C_6H_5CO-\overset{\overset{\displaystyle O\rightarrowtail}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}\rightarrowtail + \overset{\overset{\displaystyle Na}{|}}{C}_6H_5 \quad\blacktriangleright\rightarrow\quad (C_6H_5)_2C(ONa)COC_6H_5 ;$

II. $(C_6H_5)_2C(ONa)-\overset{\overset{\displaystyle O\rightarrowtail}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}\rightarrowtail + \overset{\overset{\displaystyle Na}{|}}{C}_6H_5 \quad\blacktriangleright\rightarrow$

$\qquad\qquad (C_6H_5)_2C(ONa)-C(ONa)(C_6H_5)_2.$

Sodium benzpinacone.
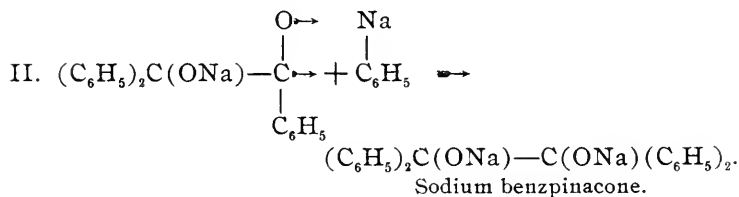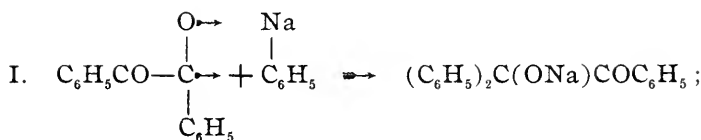
The products actually obtained in the experiments described above are phenylbenzoin (I.), benzoic acid, and triphenylcarbinol, but no benzpinacone (II.). How are these facts to be explained? The sodium phenylbenzoin (I.) dissociates into diphenylmethylene and benzoate of sodium, as has been made probable by the above experiments with phenylbenzoin. The diphenylmethylene takes up oxygen from the air, giving benzophenone, which naturally must react at once with the sodium phenyl present to give triphenylcarbinol. Furthermore, benzpinacone dissociates spontaneously into benzophenone and benzhydrol, as has been shown above in the action of sodium and brombenzene on this compound. It is, therefore, exceedingly probable that benzpinacone sodium (II.) dissociates spontaneously into benzophenone and its disodium salt,

$$\begin{array}{c}(C_6H_5)_2{=}C-O-Na\\ |\\ (C_6H_5)_2{=}CONa\end{array} = (C_6H_5)_2{=}C{=}O + \begin{array}{c}(C_6H_5)_2C-O-Na\\ |\\ Na\end{array}.$$
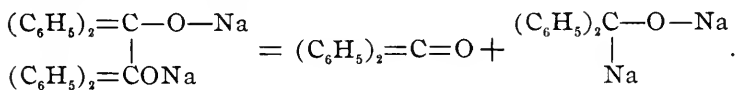
Hence, even if reaction II. takes place under the existing conditions, it is impossible to expect a formation of benzpinacone.

The Action of Sodium Phenyl on Carbon Dioxide.

Sodium phenyl was made in the usual way from 10 grams of mercury phenyl and 10 grams of sodium in ligroin (boiling-point 70° to 80°) solution. On passing dry carbon dioxide into the mixture a reaction took place with considerable evo-

lution of heat. The reaction-product was poured into water and extracted with sodium carbonate. The alkaline solution gave, when acidified, 6 grams of crude benzoic acid, which, by recrystallization, gave 4.5 grams of the pure acid, melting at 122°. When mixed with a sample of benzoic acid, the melting-point was not changed. The theoretical yield is 6.9 grams of benzoic acid. This experiment was tried three times, and in every case good yields were obtained. The action of carbon dioxide on sodium phenyl is analogous to that of carbon dioxide on sodium acetylenes,[1] sodium zinc alkyls,[2] and on phenyl aluminium chloride :[3]

$$O=C=O + Na-C_6H_5 = O : \underset{\underset{C_6H_5}{|}}{C}-ONa.$$
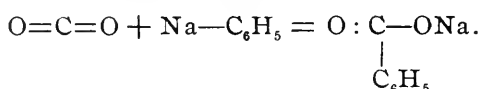
Kekulé[4] found that carbon dioxide acting upon brombenzene and sodium gave benzoic acid, diphenyl, and small amounts of benzophenone and phenyl benzoate. This shows that in a mixture of brombenzene, sodium, and carbon dioxide, the sodium first acts upon the brombenzene to give sodium phenyl. Part of the sodium phenyl reacts with unchanged brombenzene to give diphenyl, while another part reacts with the carbon dioxide to give benzoic acid.

Action of Sodium Phenyl on Chlorcarbonic Ether.

Wurtz[5] discovered that brombenzene, chlorcarbonic ether, and sodium amalgam give benzoic ether, and other homologues of brombenzene give corresponding homologues of benzoic ether.[6] The yields in all cases are very poor, as the chlorcarbonic ether gives a great deal of carbon monoxide and diethyl carbonate; mercury phenyl, etc., is also formed. It is now obvious that the sodium first reacts with the brombenzene, forming sodium phenyl, which then combines with the chlorcarbonic ether to give benzoic ether and sodium chloride.

[1] Lagermark : Ber. d. chem. Ges., **12**, 854 ; Nef : Ann. Chem. (Liebig), **308**, 281.

[2] Wanklyn : Ann. Chem. (Liebig), **107**, 125 ; **111**, 234.

[3] Friedel and Crafts : Ann. chim. phys., [6], **14**, 441.

[4] Kekulé : Ann. Chem. (Liebig) **137**, 178.

[5] Wurtz : *Ibid.*, Suppl., **7**, 125.

[6] Kekulé : Ber. d. chem. Ges., **7**, 1007 ; Jacobson : *Ibid.*, **17**, 2374 ; Nahnsen : *Ibid.*, **17**, 2192.

Five grams of mercury diphenyl in ligroin (boiling-point 60° to 80°) were converted into sodium phenyl. Three grams of chlorcarbonic ether in absolute ether were then slowly added, the solution becoming quite warm. When water was added and the solution extracted with sodium carbonate, no benzoic acid was obtained on acidifying the alkaline solution. The ligroin solution, when dried and distilled, gave only a small amount of benzoic ether, boiling at about 210°. It was identified by its odor and by conversion into benzoic acid (melting-point 118°) by means of methyl alcoholic potash. The residue from which the benzoic ether had been distilled was crystallized from alcohol, and 1.1 grams of triphenyl-carbinol, melting at 158°, were obtained. The alcohol filtrate was boiled with phenylhydrazine, but no benzophenonephenyl-hydrazone was obtained. Sodium phenyl and chlorcarbonic ether, as is obvious from the preceding, give very little benzoic ether. The benzoic ether first formed must, therefore, react further with sodium phenyl, as follows:

$$
\begin{array}{ccc}
\overset{\displaystyle O \dashrightarrow}{\underset{\displaystyle OC_2H_5}{\overset{|}{C_6H_5-C}}}{\dashrightarrow} + \overset{\displaystyle Na}{\overset{|}{C_6H_5}} & \dashrightarrow & (C_6H_5)_2\overset{\displaystyle ONa}{\overset{|}{C}}-OC_2H_5 \quad \dashrightarrow
\end{array}
$$

$$(C_6H_5)_2CO + NaOC_2H_5,$$
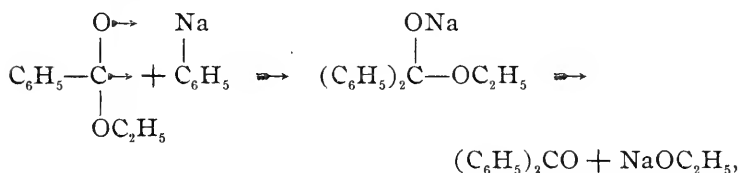
and the resulting benzophenone then reacts with more sodium phenyl, forming triphenylcarbinol. This is proved by the following experiment:

Action of Brombenzene and Sodium on Benzoic Ether.

When a solution of 3 grams benzoic ether and 6 grams brombenzene in absolute ether was allowed to stand sealed twenty-four hours with 2 grams of sodium wire, no metal was left. The solution was colored deep-blue and a blue precipitate covered the bottom of the vessel.

The reaction-products were found to be 1.4 grams triphenylcarbinol, melting at 158°, 0.2 gram of benzoic acid, 0.3 gram of triphenylmethane, melting-point 92° to 93°, and benzophenone, which was identified by means of its phenyl-

hydrazone (0.42 gram melting at 135°). In a second experiment, where the same amounts of benzoic ether and brombenzene but more sodium, 3 grams instead of 2 grams, were used, no benzoic acid was obtained. The other products were triphenylcarbinol, 1.2 grams, triphenylmethane, 0.65 gram, and benzophenone, 1.4 grams, melting at 48° to 49°. The triphenylcarbinol was separated from the other two products by crystallization from alcohol. The alcoholic filtrate, in the second experiment, gave, on fractional distillation, 2.4 grams of material boiling between 280° to 350°—a mixture of benzophenone and triphenylmethane. This was partially separated by fractional distillation and further by fractional crystallization.

Action of α-Bromnaphthalene and Sodium on Benzophenone.

α-Naphthyldiphenylcarbinol.—When 10 grams of benzophenone, 12 grams of α-bromnaphthalene, and 5 grams of fine sodium wire in absolute ether stood one week in a sealed vessel, and the mixture was treated with water and extracted with potassium hydroxide, a small amount of benzoic acid was obtained. The ether was distilled off, and the residue, by distillation with steam, gave 1 gram of naphthalene, melting-point 80°. The part not volatile with steam was dissolved in ether and ligroin, and after long standing a substance crystallized out which melted at 135° when recrystallized from ether and ligroin. It was easily soluble in ether and alcohol, but insoluble in water and ligroin.

The same compound, α-naphthyldiphenylcarbinol, was formed when 5 grams of brombenzene, 5 grams of α-naphthylphenylketone, and 2 grams of sodium wire in absolute ether stood two days. When the ethereal solution was treated with water and extracted with sodium carbonate no acid was obtained. The ethereal solution was dehydrated and distilled. The residue, crystallized from ether and ligroin, gave α-naphthyldiphenylcarbinol, melting at 135°. When samples of the two products were mixed, the melting-point was not changed.

Analysis :

I. 0.1721 gram substance gave 0.5589 gram CO_2 and 0.0952 gram H_2O.

II. 0.1912 gram substance gave 0.6192 gram CO_2 and 0.1023 gram H_2O.

	Calculated for $C_{23}H_{18}O$.	I.	Found. II.
C	89.00	88.57	88.32
H	5.86	6.14	5.95

Action of p-Bromtoluene and Sodium on Benzophenone.

Benzophenone (5 grams), *p*-bromtoluene (5 grams), and sodium (2 grams) in absolute ether stood two weeks in a sealed vessel. The solution became intensely blue and a blue precipitate was formed. When the solution was treated with water and extracted with sodium carbonate no acid was found. When the ether was evaporated off and the residue dissolved in ligroin and ether, a substance at length crystallized out which melted at 74° when recrystallized from ligroin. This is *p*-tolyldiphenylmethane.[1]

The same substance was formed when 5 grams of *p*-tolyl-phenylketone, melting-point 58°, 3 grams of brombenzene, and 2 grams of fine sodium wire in absolute ether, were allowed to stand one week. The mixture was poured into water and extracted with sodium carbonate, but no organic acid was found. When the ether was evaporated off and the residue distilled with steam, about 1 gram of brombenzene was recovered. The residue was distilled in a vacuum and 1 gram of a liquid boiling at 195° to 200°, at 12 mm., was obtained, which, upon standing, gradually solidified. This was crystallized from ether and ligroin and gave 0.5 gram of *p*-tolyldiphenyl-methane, melting at 74°. When samples of the two products were mixed, the melting-point was not changed. The yield is very poor in both cases and apparently no *p*-tolyldiphenylcar-binol is formed.

Five-tenths gram of the *p*-tolyldiphenylmethane was heated in a sealed tube with nitric acid (20 per cent) for twenty-four hours, at 150° to 160°. When the tube was opened a great

---

[1] Cf. E. and O. Fischer: Ann. Chem. (Liebig), **194**, 263.

deal of gas escaped. The product was then taken up in ether and extracted with sodium carbonate. When this alkaline solution was acidified, 0.2 gram of *p*-triphenylcarbinolcarbonic acid,[1] melting-point 200°, was obtained; this was further identified by its very insoluble barium salt.

The Action of Sodium on Ketones.

The action of sodium on carbonyl compounds, as aldehydes, ketones, acid chlorides, and acid esters has been discussed by Nef. In Liebig's *Annalen der Chemie*, **308**, 283 to 292, he presents the view that at first disodium addition-products, *e. g.*,

$$\underset{H}{\overset{C_6H_5}{>}}C-O + Na-Na = \underset{H}{\overset{C_6H_5}{>}}C-O-Na,$$
$$\underset{Na}{\big|}$$
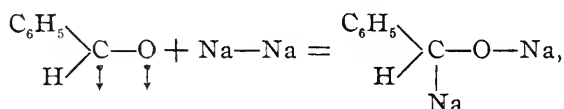
are formed which immediately react further with a second carbonyl group present in the same or in another molecule. Thus the benzil sodium of Beckmann and Paul was proved by him to be sodium dioxystilbene,

$$\begin{matrix} C_6H_5-CONa \\ \| \\ C_6H_5-CONa \end{matrix} \left(\text{from } \begin{matrix} C_6H_5C \overset{ONa}{\underset{Na}{<}} \\ | \\ C_6H_5C=O \end{matrix} \text{ by intramolecular addition} \right).$$
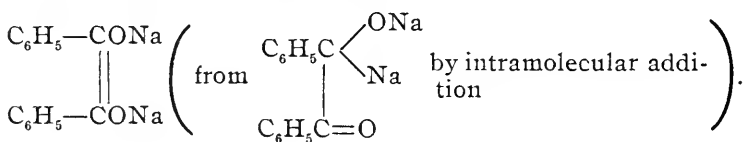
Similarly, benzophenone disodium must act with a second molecule of benzophenone,

$$(C_6H_5)_2C\overset{ONa}{\underset{Na}{<}} + \underset{\big\downarrow\ \big\downarrow}{O-C=C_6H_5} = (C_6H_5)_2\overset{\overset{ONa}{|}}{\underset{\underset{ONa}{|}}{C}}-C=(C_6H_5)_2,$$
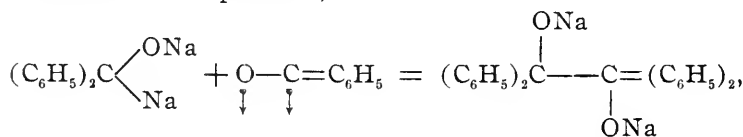
Sodium benzpinacone.

to give sodium benzpinacone. Beckmann and Paul[2] ascribe the following very improbable constitution to the product obtained by them by the action of sodium on benzophenone,

$$(C_6H_5)_2=\overset{\overset{ONa}{\diagup}}{C}-O-C\overset{Na}{\underset{(C_6H_5)_2}{<}}.$$
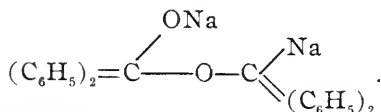
[1] Oppenheimer: Ber. d. chem. Ges., **19**, 2029.
[2] Ann. Chem. (Liebig), **266**, 9 (1891).

Their salt gives, on treatment with water, benzpinacone and equal molecules of benzophenone and benzhydrol. The relative amounts obtained vary tremendously according to the amount of water used and possibly also according to other conditions. Furthermore, their dry salt gave, on treatment with dry carbon dioxide, equal molecules of benzophenone and benzilic acid. These results are self-evident on the basis of the ideas of Nef. We have but to conclude that sodium benzpinacone dissociates at ordinary temperatures into benzophenone and benzophenone disodium,

$$(C_6H_5)_2 = C \underset{ONa}{\overset{|}{\rule{0pt}{1em}}} \underline{\hspace{2em}} C \underset{ONa}{\overset{|}{\rule{0pt}{1em}}} = (C_6H_5)_2 =$$

$$(C_6H_5)_2 = C = O + Na - C \underset{ONa}{\overset{|}{\rule{0pt}{1em}}} = (C_6H_5)_2,$$
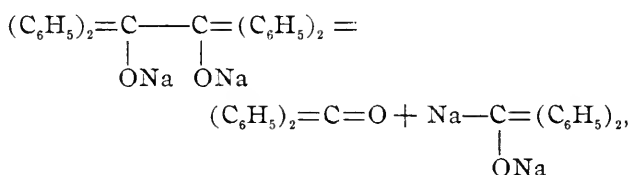
as is probable from the facts known regarding benzpinacone itself, as well as from the experiments described above with benzpinacone, sodium, and brombenzene. We must, in consequence, expect to obtain from this salt, by the action of water, varying quantities of benzpinacone and equal molecules of benzhydrol and benzophenone. With dry carbon dioxide (provided the non-dissociated salt does not act *per se*) we must obtain equal molecules of benzophenone and carboxylated benzilic acid, as follows :

$$2CO_2 + (C_6H_5)_2 = C \underset{ONa}{\overset{|}{\rule{0pt}{1em}}} \underline{\hspace{2em}} C \underset{ONa}{\overset{|}{\rule{0pt}{1em}}} = (C_6H_5)_2 =$$

$$(C_6H_5)_2 = C : O + (C_6H_5)_2 = C \Big\langle \begin{smallmatrix} O - Na \\ Na \end{smallmatrix} + 2O - C = O =$$

$$(C_6H_5)_2 = CO + (C_6H_5)_2 = C \Big\langle \begin{smallmatrix} O - C - ONa \\ \| \\ O \\ CONa \\ \| \\ O \end{smallmatrix} .$$
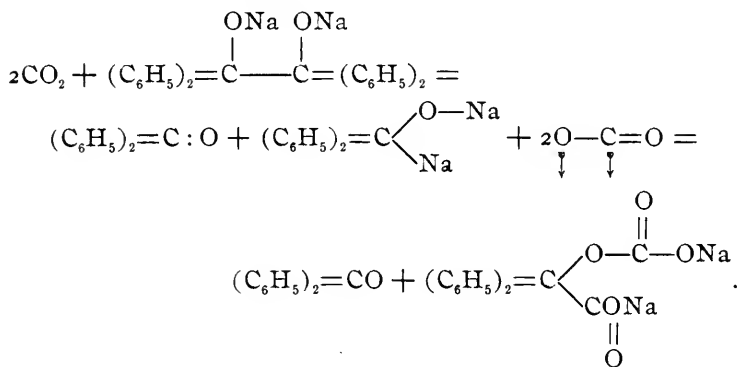
The carboxylated benzilic acid must lose carbon dioxide readily,

$$(C_6H_5)_2 = C \begin{cases} O-COOH \\ COOH \end{cases} = (C_6H_5)_2 = C \begin{cases} OH \\ COOH \end{cases} + CO_2.$$
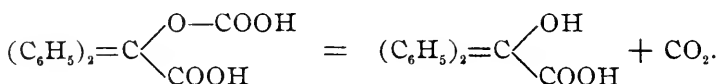
The formation of equal molecules of benzophenone and of benzilic acid in this reaction as observed by Beckmann and Paul is, therefore, easily understood. Furthermore, in continuing experiments in this direction, we have been able to prove that a carboxylated benzilic acid (oily acid, readily losing CO_2) is actually formed, thus establishing the correctness of the above conclusions.

Action of Sodium on Benzophenone.

Benzophenone (melting-point 48° to 49°, 5 grams) in absolute ether was treated with 2 grams of sodium (3 atoms) for three days. The solution became intensely blue and a blue solid was formed. The mixture was poured into water and extracted with sodium carbonate, but no organic acid was found. Upon evaporating the ether and crystallizing the residue from alcohol, 3 grams of pure benzpinacone (melting-point 185° to 186°) were obtained. By boiling the alcoholic filtrate with phenylhydrazine, only a small quantity of benzo-phenonephenylhydrazone was obtained. Upon distilling off the phenylhydrazine with steam and recrystallizing the residue from ether and ligroin, 1.6 grams of benzhydrol, melting at 66°, were obtained. Whether the large quantity of benzhydrol formed came from the action of water on benzophenone disodium,

$$(C_6H_5)_2 = \underset{\underset{Na}{|}}{C} - ONa + H_2O \longrightarrow (C_6H_5)_2 = CHOH + 2NaOH,$$
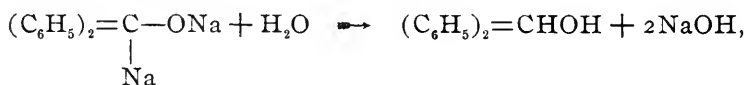
or was formed by the reduction of the benzophenone by the nascent hydrogen liberated from the excess of sodium when the reaction-mixture was poured into water, is not certain.

Analysis of benzpinacone :

0.2252 gram substance gave 0.7001 gram CO_2 and 0.1225 gram H_2O.

	Calculated for $C_{26}H_{22}O_2$.	Found.
C	85.20	84.79
H	6.07	6.04

The Action of Sodium and Carbon Dioxide on Benzophenone.

A flask containing 5 grams of benzophenone and 7 grams (11 atoms) of fine sodium wire in 100 cc. absolute ether was attached to a return-condenser through which was passed a tube leading in well-dried carbon dioxide. The flask was well shaken, and the benzophenone sodium was evidently acted on as fast as formed, for the blue color was never very intense. The mixture was poured into a separatory-funnel and water was added to dissolve the sodium salts. When the water solution was acidified, an oily acid, probably carboxylated benzilic acid, $(C_6H_5)_2 = C \diagup^{OCOOH}_{COOH}$, which did not change as long as the water was cold, was precipitated; but when the water was warmed the oil decomposed with a lively evolution of carbon dioxide, forming 3 grams of pure benzilic acid (theory 5.5 grams) that melted at 149° to 150°.

Analysis :

0.2345 gram substance gave 0.6330 gram CO_2 and 0.1132 gram H_2O.

	Calculated for $C_{14}H_{12}O_3$.	Found.
C	73.65	73.40
H	5.31	5.35

On the Isomeric Diacetyldioxystilbenes.

During the progress of Nef's work on sodium benzil and its conversion into diacetyldioxystilbene, two isomeric diacetyl-dioxystilbenes, melting at 110° and 153°, respectively, were independently discovered by Thiele.[1] We have repeated Thiele's experiments and proved that the lower melting isomer is identical with Nef's diacetyldioxystilbene, which, when perfectly pure (recrystallization from ether), melts at 118°.

The diacetyldioxystilbene of Nef has been examined crystallographically by Bowman in Groth's laboratory.[2] Two

[1] Thiele : Ann. Chem. (Liebig), **306**, 142 ; cf. Nef : *Ibid.*, **308**, 290.

[2] Nef : Ztschr. für Krystallographie ; cf. Ann. Chem. (Liebig), **308**, 290.

preparations, one made by Nef's and the other made by Thiele's method, were therefore submitted to Dr. O. C. Farrington, of the Field Columbian Museum, for comparison. His report (July 15, 1899) is as follows :

"The crystals of the two lots submitted by Mr. Acree proved to be entirely similar. They are all alike in habit, being made up of a short, stout prism, truncated to a somewhat tabular form by the prominent orthopinacoid. The orthodome d(101) is also a prominent face, while c(001) appears as a narrow face truncating the edge $a\ d$.

"As crystals of lot No. 1 had previously been measured by Bowman (*loc. cit.*) I confined my measurements to those of lot No. 2. Few faces on these crystals were suited to accurate measurement, oscillatory combinations usually causing a line of signals several degrees in length. The following measurements made on two different crystals may, however, be deemed characteristic. For comparison the values of similar angles calculated from Bowman's ratios are given :

			Measured.	Mean.	Calculated.
a' : c	=	(100) : (001)	86° 46′		
			86° 40′	86° 47′	86° 56′
			86° 55′		
a : m	=	(100) : (110)	70° 22′		
			70° 30′	70° 20′	70° 30′
			70° 8′		
m' : m''	=	(110) : (1̄10)	39°	39° 4′	39°
			39° 8′		
m : n	=	(110) : (120)	9° 20′		
			9° 40′	9° 30′	9° 28′
a : d	=	(100) : (101)	42° 25′	42° 25′	42° 25′

"The form K(102) noted by Bowman was not observed on the crystals. The calculated and measured values for the angles quoted above agree so closely that there can be no doubt that the crystals all have the same form."

Analysis of the diacetyldioxystilbenes, obtained by Thiele's method :

I. 0.2198 gram substance (melting-point 107° to 108°) gave 0.5837 gram CO_2 and 0.1139 gram H_2O.

II. 0.2191 gram substance (melting-point 118°) gave 0.5811 gram CO_2 and 0.1102 gram H_2O.

III. 0.2188 gram substance (melting-point 153°) gave 0.5848 gram CO_2 and 0.1032 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$.	I.	Found. II.	III.
C	72.92	72.43	72.34	72.89
H	5.46	5.76	5.59	5.24

I wish to thank Dr. J. U. Nef for the great inspiration and encouragement he has given me during this work.

XLI.—THE ACTION OF ZINC ON TRIPHENYL-CHLORMETHANE.

[SECOND PAPER.]

BY JAMES F. NORRIS.

A reply by M. Gomberg in the April number of this JOURNAL to a paper under the above title by Miss L. R. Culver and myself[1] contains a number of criticisms of our statements and experimental work. The reply was evidently written after a very hasty reading of the experimental evidence put forward by us, and, consequently, I hope to show that the criticisms of our experiments are not well founded, and that the suggestions put forward in explanation of our results are not in accord with the facts.

Action of Sodium.

M. Gomberg takes exception to our statement that "It was shown in the same paper that, under certain conditions, triphenylchlormethane reacts with sodium, contrary to the observations of Gomberg." This statement is true, for it was shown that while sodium is inactive toward triphenylchlormethane, dissolved in dry ether, it did react with the halogen compound if brombenzene were present. As with other halides of this type, a catalytic agent is necessary to bring about a reaction between triphenylchlormethane and sodium. Bromben-

[1] This JOURNAL, **29**, 129.

zene played this part in our experiments. We have accumulated a number of facts on the action of sodium on triphenylchlormethane, which have not been published as yet. In dry ether there is no reaction after a number of days, but if a little ethyl acetate is added a reaction soon begins between the metal and the halogen compound. In this respect triphenylchlormethane is like other alkyl halides.

Is the Reaction Quantitative?

We said in our paper, "At the beginning of the work it was found that the statement of Gomberg was incorrect, that when the reaction between zinc and triphenylchlormethane took place in benzene solution the metal reacted quantitatively according to the following equation:

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C- + ZnCl_2."$$
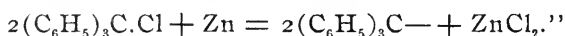
In reply, Gomberg says: "In turning to the reference made by the authors to my paper in respect to this question, we see at once that there is no such statement either made or implied. We read: 'The zinc removes the halogen from triphenylchlormethane quantitatively.'"[1] I think that a reference to Gomberg's original paper will lead one to the conclusion stated in our sentence. It was there stated that zinc removes the halogen quantitatively, and this was shown by determining the chlorine in the zinc chloride formed. The amount of chlorine removed as zinc chloride was stated in the tabulation of the results. This experiment was faulty. If all the chlorine had been converted quantitatively into zinc chloride, as claimed by Gomberg, the only thing left was, of course, the two $(C_6H_5)_3C-$ groups. This is expressed, as far as I can see, by the equation written by us. That Gomberg was of this opinion is shown by the following statement which appears later in the same paper (page 768) : "The action of zinc results, as it seems to me, in the mere abstraction of the halogen, leaving the free radical,

$$(C_6H_5)_3C.Cl + zn = (C_6H_5)_3C + znCl."$$
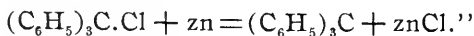
[1] J. Am. Chem. Soc., **22**, 761 (1900).

Formation of the Double Salt.

By putting together two sentences from one paragraph, without indicating that anything stood between them, Gomberg makes us say what we did not say, and then proceeds to answer it. He says that Norris and Culver say : '' During the course of the reaction a thick, dark mass separates, which Gomberg assumed to be a compound of benzene and zinc chloride. Gomberg, in a later paper, briefly mentions this mistake, but he has reported no further work to test this point.'' In our paper, after the first sentence just quoted, comes an account of Gomberg's method of determining the chlorine removed by the zinc. Then comes the following : '' The single quantitative experiment on which Gomberg based his theory in his first paper was, therefore, manifestly incorrect, and there were no data as to the amounts of zinc and triphenylchlormethane which entered into the reaction. Gomberg, in a later paper, mentions this mistake, but he has reported no further work to test this point.'' It is evident that reference was made to the relation between the amounts of zinc and triphenylchlormethane that reacted with one another, and we repeat that our paper furnishes the only data available on this important point. Gomberg also objects to the word '' single'' in the above sentence, and says that he made three determinations of the chlorine removed. He can hardly consider an endeavor to get checking results in a quantitative determination as three quantitative experiments in support of his conception of trivalent carbon.

Action of Zinc in Ethyl Acetate.

Gomberg then takes exception to our statement : '' As triphenylmethane, triphenylcarbinol, and an oil are at times present, an investigation of the cause of the formation of these substances must be made before the reaction, which is evidently a very complex one, can be exactly interpreted.'' He states that he had already shown that these substances are formed, but admits that he had not explained the cause of their presence. He says : '' It remains, however, to determine whether these products are formed before or during the

oxidation of the unsaturated hydrocarbon.'' It was in an attempt to find an explanation of these facts, which it seemed to us must be understood before the reaction is cleared up, that we undertook a quantitative study of the reaction.

The criticisms of our experimental results and their interpretation, which then follows, seem to me to be wholly valueless. In regard to the large amount of zinc which we found was used in the reaction, Gomberg suggests that the conclucl usions drawn are falsified by the fact that zinc oxide was produced, as he says, '' by the direct oxidation of the metal by the oxygen, under the influence of the different products present.'' The amount of zinc oxide formed was determined and found to be so small that it was not taken into account in the calculation of the results. It is also suggested in a footnote that zinc may be soluble in a solution of zinc chloride in ethyl acetate. In one experiment reported in our first paper, Gomberg's equation required for the triphenylchlormethane used 0.127 gram of zinc, whereas 0.252 gram entered into the reaction. According to Gomberg, a 10 per cent solution of zinc chloride in ethyl acetate dissolved but 0.035 gram of zinc (from how much is not stated) in five days and 0.066 gram in two weeks. In our experiment about 1 gram of zinc was present during the reaction, which was shown to be complete in ten days. The dilution was such that had all the chlorine been present at the end of the reaction as zinc chloride, the solution would have been one of about 1 per cent. It seems to me, therefore, that Gomberg has suggested no explanation which can be considered helpful, of the large amount of zinc which reacts with triphenylchlormethane. The fact that so much of the metal does enter into the reaction is of vital importance, when the reaction is to be completely understood.

While zinc may be dissolved by a solution of the ordinary zinc chloride dissolved in ethyl acetate, as claimed by Gomberg, our experimental results lead us to the conclusion that it is not acted upon by the pure chloride produced by the action of the metal on an organic chloride dissolved in pure ethyl acetate. An experiment with benzophenone chloride gave positive evidence on this point. About 9 grams of the

chloride, dissolved in 25 cc. of ethyl acetate, were shaken with 10 grams of zinc for a number of days. As long as any benzophenone chloride was present, the solution had a dark green color due to the presence of a compound of the ketone chloride and zinc chloride. After shaking for 5 days the reaction was complete, as the solution had become colorless. The mixture was shaken for eight more days in order to determine whether the zinc present (about 7.6 grams) would be dissolved by the zinc chloride formed in the reaction (about 5 grams). A determination of the zinc which remained showed that 2.47 grams had reacted, whereas the amount required by the equation

$$2(C_6H_5)_2CCl_2 + 2Zn = (C_6H_5)_2C = C(C_6H_5)_2 + 2ZnCl_2$$

was 2.56 grams. It is evident, therefore, that the zinc chloride had dissolved no zinc, and that Gomberg's explanation of the large amounts used in our experiments with triphenylchlormethane is not in accord with the facts.

Absorption of Oxygen.

Gomberg's statement that the conclusion drawn by us from the large amount of oxygen absorbed is invalidated by the fact that zinc oxide was formed, is again not in accord with the facts. In some of the experiments the amount of zinc oxide formed was determined. Experiment 4, given in our first paper, can be taken as an example. The amount of zinc used was 0.417 gram, whereas 0.248 gram is required by Gomberg's statement, that the chlorine is removed quantitatively as zinc chloride. In this experiment 0.098 gram of oxygen was absorbed, whereas the peroxide obtained contained only 0.046 gram. The zinc oxide was determined and found to be 0.012 gram. This contains about 0.003 gram of oxygen, which is such a small quantity that it is almost negligible in comparison with the difference between the oxygen in the peroxide and the total absorbed in the reaction—0.052 gram. The data about the quantities of zinc oxide formed were not published in our former paper, as the amounts were small, and as it had not been determined whether the oxide was formed during the oxidation of the unsaturated com-

pounds, or when the solution was brought into contact with the moisture of the air. The fact remains that the amounts were so small that it was not considered necessary to introduce them into the calculations. The criticism of Gomberg of our results is, therefore, of no value.

Gomberg also points out that no reference was made to his observation that triphenylmethyl absorbs about 14 per cent more than the theoretical quantity of oxygen in going over to the peroxide. Our observations are of an entirely different nature, for in our experiments from two to three times the theoretical amounts were absorbed by the solution in which the reaction between triphenylchlormethane and zinc took place. We were evidently dealing with a different reaction from the one studied by Gomberg, when the excess was only about one-seventh of the whole. The results do warrant us, therefore, in believing that we have observed a reaction overlooked by Gomberg.

The Yield of the Peroxide.

Gomberg points out under this title that our results in different experiments are not uniform, that we did not obtain the same amount of peroxide in each case, and that, as a consequence, no conclusions can be drawn. The point is not well taken. While the yield of the peroxide did vary greatly, this variation was always accompanied by a corresponding variation in the amounts of zinc used and the other products formed. As the percentage of peroxide decreased the amounts of zinc used and carbinol formed increased. The results are not chance ones, and the variation of which Gomberg complains takes place with all the substances involved, in such a way that they help us in interpreting the reaction.

Gomberg states gratuitously (page 370) : ''As the authors did not assure themselves that the action of zinc on triphenylchlormethane was carried to the end, etc.'' It is clearly stated in our first paper how we determined when the reaction was complete. In describing our experiments we said : ''At first the gas was absorbed quite rapidly, but toward the end of the experiment the absorption was very slow.

The yellow color of the solution slowly decreased until it had almost entirely disappeared, when the reaction was complete. When the absorption ceased the flask was removed and the zinc left determined.'' The data on the rate of absorption in in each experiment reported are at hand. When, after standing twenty-four hours, there was no further decrease in the volume of oxygen, it was plain that the reaction was complete. In our experiments the reaction was allowed to proceed for eight to fourteen days. Gomberg also asks, '' What precautions were taken to prevent the zinc from becoming coated with a layer of the insoluble triphenylmethyl peroxide?'' This possible source of error was, of course, looked after.

A criticism then follows which could not have been written had our quantitative results been examined. Gomberg, in attempting to explain the presence of triphenylcarbinol, makes this statement : '' Still, as the authors did not assure themselves that the action of zinc on triphenylchlormethane was carried to the end, *i. e.*, that all the halogen compound was attacked by the metal, and as they treated the reaction-product with water, it is evident that any unchanged triphenylchlormethane would be converted by this treatment into the triphenylcarbinol.'' According to this '' explanation'' of the high yield of carbinol, the latter is produced by the action of water on the triphenylchlormethane which had not entered into reaction with zinc. If this view is correct, it follows that less than the theoretical amount of zinc also reacted, as it is assumed that the reaction was incomplete. The results published in our paper prove that this is not the case. The largest yield of carbinol was obtained when the *largest* amount of zinc was used. In Experiment 2, described in our paper, nearly twice the amount of zinc required by Gomberg's equation entered into the reaction, a_ ' vet a large percentage of carbinol was obtained. The experimental results show that Gomberg's attempt to find a source of error in our work is unsuccessful.

From the above it will be seen, I think, that Gomberg's criticisms and suggestions are entirely inconsistent with one another. In order to explain the large amount of zinc used,

he suggests that the metal was dissolved by the zinc chloride formed in the reaction, and was oxidized to zinc oxide by the oxygen present. In order to explain the formation of the large amount of triphenylcarbinol found in the same experiment, when the zinc used is far in excess of the theoretical amount calculated from his conception of the reaction, he assumes that the reaction was incomplete, and that the metal was coated with the precipitated peroxide, and so prevented from entering into reaction. These views could not have been put forward if the results published by us had been thoroughly studied.

In conclusion, I can say that I believe that not a single point brought out by Gomberg in his last paper has a bearing on our experimental work and conclusions, and that I still believe that these results show that in ethyl acetate solution the reaction between zinc and triphenylchlormethane is a very complicated one.

Boston, April 8, 1903.

REVIEWS.

PRINCIPLES OF INORGANIC CHEMISTRY. By HARRY C. JONES, Associate Professor of Physical Chemistry in Johns Hopkins University. New York : The Macmillan Co. 1903. pp. xx + 522. Price, $4.00.

The qualities of the style of the prolific and enthusiastic writer of this work are too well known to need detailed review at this time. The work under review has the highly commendable object of presenting the facts of inorganic chemistry in a systematic manner, with the help of the recent laws and theories of physical chemistry. As the master, van't Hoff, has pointed out, inorganic chemistry acquires its greatest interest and significance when treated in this way. The problem is not altogether an easy one, because it involves the interweaving of a double classification. In this work the writer has wisely used the periodic system as the first basis of the arrangement, and has introduced the modern ideas where they seemed most likely to be useful. The periodic system itself is not explained until three typical elements, oxygen, hydrogen, and chlorine, have been studied in detail. The discussion of Faraday's Law, the Phase Rule, and the Law of "Mass-Action" are taken up at the first opportunity, so that they may be useful in classifying subsequent facts. Of-

ten the generalization is very opportune, but occasionally it must be confessed that the bodily transfer of pages from the author's work on physical chemistry is evident.

As every one knows, it is almost impossible to write a book which shall be free from errors, and this one shares the common lot. On page 10, Proust, of Angers, is spoken of as an Englishman ; on page 86, an impracticable apparatus is depicted, and there are a few mistakes in proof-reading which affect important figures or symbols. A more serious defect than these trivial points seems to me, however, an occasional lack of clearness in the distinction between fact and hypothesis. This is perhaps best illustrated by a quotation from page 71 : '' The hypothesis of Avogadro has been confirmed by such an abundance of subsequent work, in so many directions, that it is now placed among the well established laws of nature.'' This somewhat doubtful attitude is not merely a matter of words ; it seems to penetrate the thought as well, at times. One of its results is the occasional tendency to overlook the exceptions or difficulties attending many hypotheses; for example, a beginner would probably leave the book with the idea that the hypothesis of ionization is a perfect theory which leaves nothing unexplained. The reviewer does not mean hereby to discourage the use of hypotheses but merely wishes to emphasize the importance of realizing their hypothetical nature.

One sees with regret the retention of Trevor's polyglot nomenclature for degrees of freedom, and hopes that in a subsequent edition the purely Latin form of this nomenclature suggested by the reviewer five years ago and more recently adopted by Trevor himself, may be substituted. On the other hand, one sees with pleasure the adoption of oxygen as the standard of atomic weights, and in many other cases, where there is a choice between two paths, the right one seems to have been taken. There is but one index, giving both authors and subjects, and no references to the original sources of the information are recorded. One unusual omission should perhaps be mentioned, the specific gravities of solids and liquids are very rarely stated.

All things considered, the book is interesting and will probably be useful and render inorganic chemistry good service by inciting the inorganic chemist to think about the general bearings of the facts with which he deals.   T. W. R.

UEBUNGSBEISPIELE FÜR DIE ELEKTROLYTISCHE DARSTELLUNG CHEM-
ISCHER PRÄPARATE, ZUM GEBRAUCH IM LABORATORIUM FÜR CHEM-
IKER UND ELEKTROCHEMIKER. Von DR. KARL ELBS, o. Professor
und Direktor des Laboratoriums für physikalische und organische
Chemie an der Universität Giessen. Mit 8 Abbildungen im Text.
Druck und Verlag von Wilhelm Knapp. Halle, a. s. 1902. pp. 100.

This little book gives a clear and concise account of meth-
ods for preparing electrolytically some of the more important
inorganic and organic compounds. The first part deals with
the electrical apparatus which is necessary for such work.
This is followed by a description of methods for the prepara-
tion of a number of salts of sodium and potassium.

The latter part of the book, dealing with organic synthesis,
is much wider in its scope. As is well known, electrolytic
synthesis in organic chemistry has to do chiefly with the aro-
matic compounds. This fact is made evident by the little
work in hand, which will doubtless prove to be useful in con-
nection with the new and interesting applications of electro-
chemistry and organic chemistry.   H. C. J.

HANDBUCH DER ELEKTROCHEMIE. Bearbeitet von PROF. DR. BORCH-
ERS, Aachen; PRIVATDOCENT DR. E. BOSE, Göttingen; PRIVATDOCENT
DR. H. DANNEEL, Aachen ; PROF. DR. R. ELBS, Giessen ; PROF. DR.
F. KÜSTER, Clausthal ; BERGINGENIEUR F. LANGGUTH, Mechernich;
PROF. DR. W. NERNST, Göttingen ; und PROF. DR. H. STOCKMEIER,
Nürnberg. Verlag von Wilhelm Knapp. Halle, a. s. 1903.

According to the announcement the " Handbuch der Elek-
trochemie" is to be an elaborate treatise on this very important
chapter in physical chemistry. The work aims to cover the
whole field of electrochemistry from both the scientific and
technical standpoints, and from the staff of authors, will un-
doubtedly be a masterpiece.

The parts which have appeared thus far are : " Elektro-
magnetische Aufbereitung," by F. Langguth, and " Specielle
Elektrochemie," by H. Danneel. The " Theoretische Elek-
trochemie," will be written by Prof. Dr. W. Nernst; " Mess-
kunde," by Dr. E. Bose ; " Elemente und Akkumulatoren,"
by Prof. Dr. K. Elbs ; " Elektroanalyse," by Prof. Dr. F.
Küster ; " Anorganisch-elektrochemische Technik," by
Prof. Dr. W. Borchers ; " Organisch-elektrochemische Tech-
nik," by Prof. Dr. K. Elbs ; and " Galvanotechnik," by Dr.
H. Stockmeier.

The work ought to be in every public scientific library, as
well as in the libraries of individuals who are interested in
any phase of electrochemistry.   H. C. J.

INDEX TO VOL. XXIX.

AUTHORS.

SUBJECTS.

FORMULAS.

C_2-GROUP.

2 IV.

C_3-GROUP.

3 III.

3 IV.

C_4-GROUP.

4 III.

4 IV.

4 V.

C$_5$-GROUP.

5 III.

5 IV.

C$_6$-GROUP.

6 III.

6 IV.

6 V.

C_9-GROUP.

9 III.

9 IV.

C_{10}-GROUP.

C_{11}-GROUP.

11 II.

11 III.

11 IV.

C_{12}-GROUP.

12 II.

21 IV.

C_{23}-GROUP.

23 IV.

C_{26}-GROUP.

26 II.

C_{27}-GROUP.

C_{28}-GROUP.

C_{36}-GROUP.

C_{42}-GROUP.